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PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, The Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for development of needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for programs to develop control technology for a large number of operations (greater than 500) in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient need for emissions reduction. This report contains data necessary to make that decision for the water discharges resulting from the production of nitrogen fertilizer.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of the nitrogen fertilizer industry, Dr. R. A. Venezia served as EPA Task Officer.

ABSTRACT

This report describes a study of waterborne pollutants from the manufacture of nitrogen fertilizers. It includes an evaluation of the ammonia, ammonium nitrate, and urea manufacturing processes, as well as the nitric acid process, which supplies acid to the ammonium nitrate process.

Synthetic ammonia is commonly produced in the United States by the catalytic reforming of natural gas using a six-step process. Nitric acid solution is produced in a three-step ammonia oxidation process where ammonia is catalytically oxidized to NO, and further oxidized to NO_2. NO_2 then reacts with water to form HNO_3 and NO. Ammonium nitrate solution is produced by an exothermic reaction of ammonia and nitric acid. The product ammonium nitrate solution is sold, mixed with other fertilizers, or converted to a solid form by various processes. Urea is produced in a two-step reaction in which ammonia and carbon dioxide react to form ammonium carbamate which is then dehydrated to form urea and water.

Water effluents in a nitrogen fertilizer plant originate from a variety of point and nonpoint sources. The major components in the effluents are ammonia nitrogen, nitrate nitrogen, and organic nitrogen. Low concentrations of other constituents may also be present. The potential environmental impact of nitrogen fertilizer effluents was evaluated by comparing the concentration of a particular pollutant in a receiving stream as a result of discharge to an acceptable concentratio (hazard factor). The ratio of these two values is the source severity.

Source severities were calculated for plants producing ammonium nitrate, urea, and both ammonium nitrate and urea. The constituents considered were un-ionized ammonia nitrogen (NH_3°-N), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), and organic nitrogen (ORG-N). Source severities were calculated at low and mean receiving water flow rates at receiving water pH's of 7.6 and 9. At a mean receiving water flow rate and the average pH of 7.6, ammonium nitrogen (NH_4^+-N) was responsible for the highest average source severity among the ammonium nitrate, urea, and combined ammonium nitrate-urea source types; 5.9×10^{-3}, 1.5×10^{-4}, and 1.1×10^{-2}, respectively.

Control technologies are available and in use at some nitrogen fertilizer plants. These technologies include containment, steam stripping, air stripping, urea hydrolysis, biological treatment, ion exchange, and condensate reuse.

This report was submitted in partial fulfillment of Contract 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study covers the period August 1977 to October 1978, and work was completed as of October 1978.

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ABBREVIATIONS AND SYMBOLS

aq -- denotes compound in aqueous solution
AN -- ammonium nitrate
C_{AN} -- fraction of nitrogen in ammonium nitrate (0.47)
C_D -- concentration of a particular pollutant, g/m^3
$C_{D_{AN}}$ -- concentration of given pollutant in ammonium nitrate discharge, g/m^3
C_{D_U} -- concentration of given pollutant in urea discharge, g/m^3
C_U -- fraction of nitrogen in urea (0.35)
ΔH -- change in enthalpy; the heat absorbed by a process conducted at constant pressure, KJ/mole
F -- hazard factor for particular pollutant, g/m^3
g -- denotes compound in gas phase
ℓ -- denotes compound in liquid phase
LCA -- Louisiana Chemical Association
LD_{50} -- lethal dose of a test material that causes death in 50% of a population which has ingested the material or into which the material has been injected
n -- number of samples
NH_3-N -- ammonia nitrogen including both ionized and un-ionized forms
NH_3°-N -- un-ionized ammonia nitrogen
$NH_3\text{-}N_{AN}$ -- ammonia nitrogen discharged from the ammonium nitrate plant, metric tons/day
$NH_3\text{-}N_T$ -- total discharged ammonia nitrogen, metric tons/day
$NH_3\text{-}N_U$ -- ammonia nitrogen discharge from the urea plant, metric tons/day
NH_4^+-N -- ammonium nitrogen
NO_3^--N -- nitrate nitrogen
ORG-N -- organic nitrogen
$ORG\text{-}N_U$ -- organic nitrogen discharge from the urea plant, metric tons/day
P_{AN} -- weight of product ammonium nitrate per time, metric tons/day
P_U -- weight of product urea per time, metric tons/day
PN_{AN} -- weight of product nitrogen in ammonium nitrate form per time, metric tons/day
PN_U -- weight of product nitrogen in urea form per time, metric tons/day

PN_T -- total weight of product nitrogen per time, metric tons/day
s -- standard deviation
S -- source severity for particular pollutant
T -- temperature, °C
TKN -- total Kjeldahl nitrogen, metric tons/day
TSS -- total suspended solids, including organic or inorganic particles physically held in suspension
V_D -- wastewater effluent flow rate, m^3/s
$V_{D_{AN}}$ -- volumetric flow rate from ammonium nitrate plant, m^3/s
V_{D_T} -- volumetric flow rate from total plant, m^3/s
V_{D_U} -- volumetric flow rate from urea plant, m^3/s
V_R -- volumetric flow rate of receiving body above plant discharge, m^3/s
w_i -- plant output corresponding with X_i, metric ton/day
w_j -- plant output, metric tons/day
$\bar{x}$ -- arithmetic mean
x_i -- individual of a column of numbers for which a statistical parameter is being calculated

SECTION 1

INTRODUCTION

Nitrogen fertilizers are those fertilizers whose main nutrient contribution to the soil environment is nitrogen. For the purposes of this study this definition is further restricted to the primary nitrogen fertilizers from which all other nitrogen fertilizers are derived; i.e., synthetic ammonia, ammonium nitrate, and urea, with a consideration of nitric acid as an adjunct process to that for ammonium nitrate. Production of all of these fertilizers often occurs at a single plant location. Therefore, this report characterizes entire plants as well as individual processing streams.

This study is an assessment of those water effluents released to the environment from nitrogen fertilizer plants. It describes the many manufacturing processes for each of the basic nitrogen fertilizers and identifies effluent sources. Operating parameters are presented when available. Effluent parameters are compiled and used to evaluate the impact of the nitrogen fertilizer industry on the aquatic environment. Effluent factors, concentrations, and source severities for the several processes as well as for a composite plant are given.

One section of the report discusses water pollution control technology available to the industry or under development. Major technologies such as hydrolysis and ion exchange are described at greater length, including operating parameters and degree of application when available.

The final section considers projected industry growth trends and discusses the potential impact of controls and growth on effluent quality. Emerging technologies in several of the processes are also presented in this section.

SECTION 2

SUMMARY

This report is an assessment of the water effluents released to the environment during production of nitrogen fertilizers. It includes the three major manufacturing processes of ammonia, ammonium nitrate, and urea, as well as the adjunct nitric acid process that supplies acid to the ammonium nitrate process. Excluded from study were the many blends of nitrogen fertilizers with other components, e.g., micronutrients and phosphorus, even though nitrogen may be their major nutrient. Studies on bulk blending of fertilizers and the production of the various phosphate fertilizers have been reported in other source assessment documents. Studies on air emissions from the production of ammonia, ammonium nitrate, and urea have also been published. A conceptual diagram of the nitrogen fertilizer industry is shown in Figure 1.

Production statistics for the subject compounds are shown in Table 1. The ammonium nitrate and urea produced were sold as both solid and liquid. Approximately 80% of the synthetic ammonia produced was used in the manufacture of other nitrogen fertilizers or as a direct application fertilizer. In addition, approximately 84% of the nitric acid produced was used to produce ammonium nitrate.

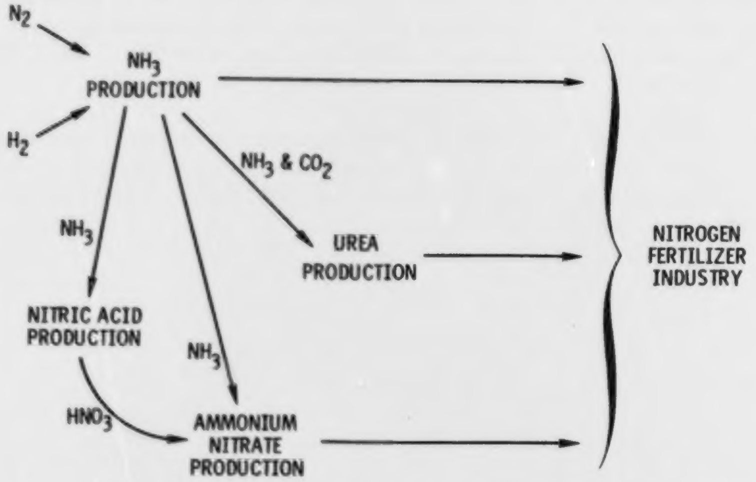

Figure 1. Conceptual diagram of the nitrogen fertilizer industry.

TABLE 1. NITROGEN FERTILIZER PRODUCTION IN THE UNITED STATES (metric tons)

Compound	Quantity produced
Ammonium nitrate (1976)	7.6×10^6
Urea (1975)	3.45×10^6
Ammonia (1976)	15.2×10^6
Nitric acid (1976)	7.16×10^6

A nitrogen fertilizer plant may incorporate one or more of the three major processes. If ammonium nitrate is produced, a nitric acid plant will commonly be on site. A consideration of the three major processes reveals that 18% of the plants manufacture two out of the three fertilizers while 23% have facilities to produce all three products.

In the United States 98% of the synthetic ammonia is produced by the catalytic reforming of natural gas using a six-step process: 1) natural gas desulfurization, 2) catalytic steam reforming, 3) carbon monoxide shift, 4) carbon dioxide removal, 5) methanation, and 6) ammonia synthesis. The other 2% of production obtains feedstock hydrogen from electrolysis cells in chlorine-caustic soda plants.

Ammonium nitrate solution is produced by an exothermic reaction of ammonia and nitric acid. The solution may be sold directly or blended with other fertilizer solutions (approximately 39% of the solution produced), or converted into solid form (approximately 61% of the solution produced). Solids are made by prilling, granulation, or graining. Prilling is the most common method of solidification, accounting for 92% of the solids produced.

Urea is produced by a two-step reaction. In the first reaction ammonia and carbon dioxide react to form ammonium carbamate. In the second reaction the ammonium carbamate is dehydrated to form urea and water. Thirty-eight percent of the urea solution produced is sold as blending agent for other fertilizers or as a raw material in the synthesis of other chemicals. The remaining 62% is solidified by either granulation or prilling. Granulation is the most common method of solid urea production, accounting for 85% of the solid product.

Nitric acid is produced in a three-step ammonia oxidation process: 1) ammonia is oxidized to nitrogen oxide (NO) or nitrogen (N_2) in the presence of oxygen and a platinum catlyst, 2) NO is further oxidized to nitrogen dioxide (NO_2), and 3) NO_2 reacts with water to form nitric acid and NO. The resulting solution stream is between 55% and 65% nitric acid.

Effluents in a nitrogen fertilizer plant originate from both point and nonpoint sources. Point sources exist at those plants where process exhaust streams are condensed instead of being released directly to the atmosphere. Condensates from evaporators and concentrators fall into this category. Cooling tower blowdown, crystallizer filtrate, and discharge from water treatment units are other examples of effluent point sources.

Nonpoint sources may be either process specific or nonprocess specific. Process specific nonpoint sources include valve and pump leaks, cooling tower overflows, shipping areas, other random spills and leaks, and plant washdowns. Nonprocess specific sources result in an effluent that cannot be traced to a particular process or specific area. Typical examples of nonprocess specific sources are general plant cleanup and runoff from precipitation. In addition, ammonia that is present in the air around a plant may be absorbed by any water stream that is open to the atmosphere.

The basic components in the effluent from a nitrogen fertilizer plant are ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3^--N), and organic nitrogen (ORG-N). Ammonia exists in both the unionized (NH_3°-N) and ionized form (NH_4^+-N), and each one is evaluated separately in terms of its potential environmental impact. The organic nitrogen is primarily urea, but there may be other organic nitrogen compounds in the stream, such as monoethanolamine from ammonia manufacture. In addition to these basic components there may be low concentration of methanol, carbon dioxide, micronutrients, or cooling tower treatment compounds in the plant effluent. These compounds are present in much lower quantities than are the major nitrogen compounds. Average effluent factors for the major compounds are given in Table 2. A compilation of effluent data from all reporting plants is given in Appendix B.

TABLE 2. AVERAGE EFFLUENT FACTORS FROM NITROGEN FERTILIZER PROCESSES (g effluent component/kg product)

	Process		
Effluent component	Ammonium nitrate including ammonia and nitric acid	Urea including ammonia	Composite plant[a,b]
NH_3-N	0.862	0.756	0.809
NO_3-N	0.471	0	0.236
ORG-N	0	0.275	0.138

[a] For plant with equal ammonium nitrate and urea capacities.

[b] Plant includes ammonium nitrate, urea, ammonia and nitric acid.

In order to evaluate the potential impact of nitrogen fertilizer plants on the environment, the source severity for the 22 plants with adequate available data was calculated. Source severity compares the concentration of a particular pollutant in a receiving stream as a result of discharge to an acceptable concentration (hazard factor). Severities were calculated based on the mean river flow rate at each plant site, the average receiving water pH of 7.6, and the average receiving water temperature of 16°C. Table 3 presents average severity values and ranges for three plant types: plants producing ammonium nitrate (including nitric acid and ammonia), plants producing urea (including ammonia), and plants producing ammonium nitrate and urea (including nitric acid and ammonia). Severities in terms of other receiving water characteristics are presented in Section 4. The wide range of severities reflects the wide range in individual plant effluent rates and receiving stream flow rates. Effluent rates vary with the degree of wastewater treatment and with the level of water recycle and reuse.

TABLE 3. AVERAGE SOURCE SEVERITIES FOR NITROGEN FERTILIZER PLANTS BASED ON MEAN RECEIVING BODY FLOW RATES

average receiving water pH = 7.6
average receiving water temperature = 16°C

Process	Effluent species	Severity	
		Average[a]	Range
Ammonium nitrate, including nitric acid and ammonia	NH_3°-N	3.0×10^{-3}	0 to 1.42
	NH_4^+-N	5.9×10^{-3}	0 to 2.80
	NO_3^--N	4.4×10^{-4}	0 to 3.3×10^{-1}
Urea, including ammonia	NH_3°-N	7.7×10^{-5}	1.2×10^{-5} to 1.1×10^{-4}
	NH_4^+-N	1.5×10^{-5}	2.3×10^{-5} to 2.2×10^{-4}
	ORG-N	2.0×10^{-5}	4.9×10^{-6} to 4.5×10^{-5}
Composite plant, including ammonium nitrate, urea, nitric acid, and ammonia	NH_3°-N	7.4×10^{-3}	1.4×10^{-5} to 7.24
	NH_4^+-N	1.1×10^{-2}	2.8×10^{-5} to 13.5
	NO_3^--N	5.1×10^{-4}	$<10^{-6}$ to 1.3×10^{-1}
	ORG-N	1.2×10^{-3}	1.4×10^{-5} to 6.5×10^{-2}

[a] Plants with low receiving stream flow rates (<1 m^3/s) were excluded from the average because they skew the data and give an inaccurate view of the total industry.

Effluent control in the nitrogen fertilizer industry is a two-step process consisting of both containment and treatment. First the many nonpoint sources must be gathered together before treatment. Containment is used to some degree at almost every nitrogen fertilizer plant, either to hold small pump leaks or to drain an entire area. Newer plants are installing extensive drainage systems and older plants are incorporating them in remodeling plans.

Treatment itself varies with effluent and composition, and even for a general treatment category there are many individual plant modifications. Steam stripping is used extensively in the production of ammonia to remove ammonia and methanol from waste streams and to a limited extent in urea production. Air stripping of ammonia has been tested but is only employed at one ammonia plant to remove ammonia from process condensate. To treat urea in waste streams, thermal hydrolysis is being promoted. Several plants have installed and are operating thermal hydrolysis systems. Biological treatment of ammonium nitrate wastes is practiced to a limited extent. Ion exchange under the name of CHEM-SEPS® is currently in use or under installation in at least 10 plants. Some plants are using an ion exchange concept based on an internally developed design.

Growth of ammonia, ammonium nitrate, and nitric acid production has been fairly constant in recent years and is projected to remain so. Urea, however, has experienced dramatic growth increases in recent years. The annual growth rate for each industry based on actual and predicted production from 1975 through 1980 is as follows:

Ammonia	5.2%
Ammonium nitrate	3.8%
Urea	9.7%
Nitric acid	1.0%

Effluent quality is expected to improve as this growth occurs for two reasons: 1) government regulations will require older plants to apply control technology, and 2) as growth occurs new plants or plant expansions will integrate control technology into overall design. The exact effect this will have on effluent quality, however, cannot be predicted.

SECTION 3

SOURCE DESCRIPTION

NITROGEN FERTILIZER MATERIALS

A nitrogen fertilizer can be defined as any fertilizer whose main nutrient contribution to the soil environment is nitrogen. Many materials fall under this definition, but most of them arise from three primary compounds: ammonium nitrate, urea, and ammonia. These three chemicals are the focus of this report. In addition, nitric acid is included as an essential part of nitrogen fertilizer materials because it is a precursor for ammonium nitrate production. All other nitrogen fertilizers are formed by combinations of or additions to these major chemicals.

Ammonium nitrate is a white crystalline material at normal temperatures. Its major end use is as a fertilizer either in liquid or solid form. Of the 7.6 x 10^6 metric tons[a] produced in 1976, 6.3% was sold directly as a liquid, 27.7% was used as a liquid in other fertilizers, 50.4% was sold as a solid fertilizer, and 15.6% was consumed in other ways; e.g., in explosives (1).

Urea is a colorless crystal at normal temperatures. Its major use is as a fertilizer with approximately 85% of production being used in this capacity(2). The remaining 15% is used as an industrial feedstock for urea-formaldehyde resins, melamine, or other products (2). In 1975, 3.45 x 10^6 metric tons of urea were produced (as 100% urea) (2).

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[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented at the end of this report.

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(1) Search, W. J., and R. B. Reznik. Source Assessment: Ammonium Nitrate Production. EPA-600/2-77-107i, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1977. 78 pp.

(2) Search, W. J., and R. B. Reznik. Source Assessment: Urea Manufacture. EPA-600/2-77-107ℓ, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977. 94 pp.

In 1976, 15.2 x 10^6 metric tons of ammonia were produced in the United States (3). Approximately 80% of this amount was used either as a direct application fertilizer or in the production of ammonium nitrate, urea, and ammonium phosphates for fertilizer application (3). The remainder was used in nonfertilizer production of ammonium nitrate, urea, nitric acid (which may in turn go to fertilizer production), acrylonitrile, and amines (3).

In 1976, 7.16 x 10^6 metric tons of nitric acid were produced in the United States (4). By material balance, approximately 84% of this production was consumed in the production of ammonium nitrate. The remainder was sold directly as nitric acid or used in other applications.

NITROGEN FERTILIZER PLANTS

Nitrogen fertilizers are often made at a complex in which more than one fertilizer product is manufactured. This type of arrangement results from the potential interrelationships shown in Figure 2. By taking advantage of these interrelationships and judicious location of manufacturing lines, plant operators can gain an economically favorable position. Cost savings are realized from minimal external purchase and transportation of raw materials and from energy savings obtained by interconnecting heat exchangers. However, all or none of these interrelationships may exist at any given plant.

Integration within the nitrogen fertilizer industry is illustrated in Figure 3 for ammonium nitrate, urea, and ammonia processes. For example, 10% of the nitrogen fertilizer plants contain only ammonia and urea production facilities. Ammonia, ammonium nitrate, and urea production facilities are contained in 23% of the plants. Nitric acid plants were assumed to exist at all ammonium nitrate facilities. Data on the various plants used in preparing Figure 3 are presented in Table A-1 in Appendix A.

This communal arrangement presents serious ramifications in the water effluent area. Many plants have common outfalls; i.e., all processes discharge their effluent into a single channel. Also discharging into the channel may be groundwater runoff or plant washdown. The problems posed by this situation will be discussed at greater length in Appendix B.

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(3) Rawlings, G. D., and R. B. Reznik. Source Assessment: Synthetic Ammonia Production. EPA-600/2-77-107m, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977. 83 pp.

(4) Current Industrial Reports, Inorganic Chemicals, 1976. M28A(76)-14, U.S. Department of Commerce, Washington, D.C., August 1977. p. 16.

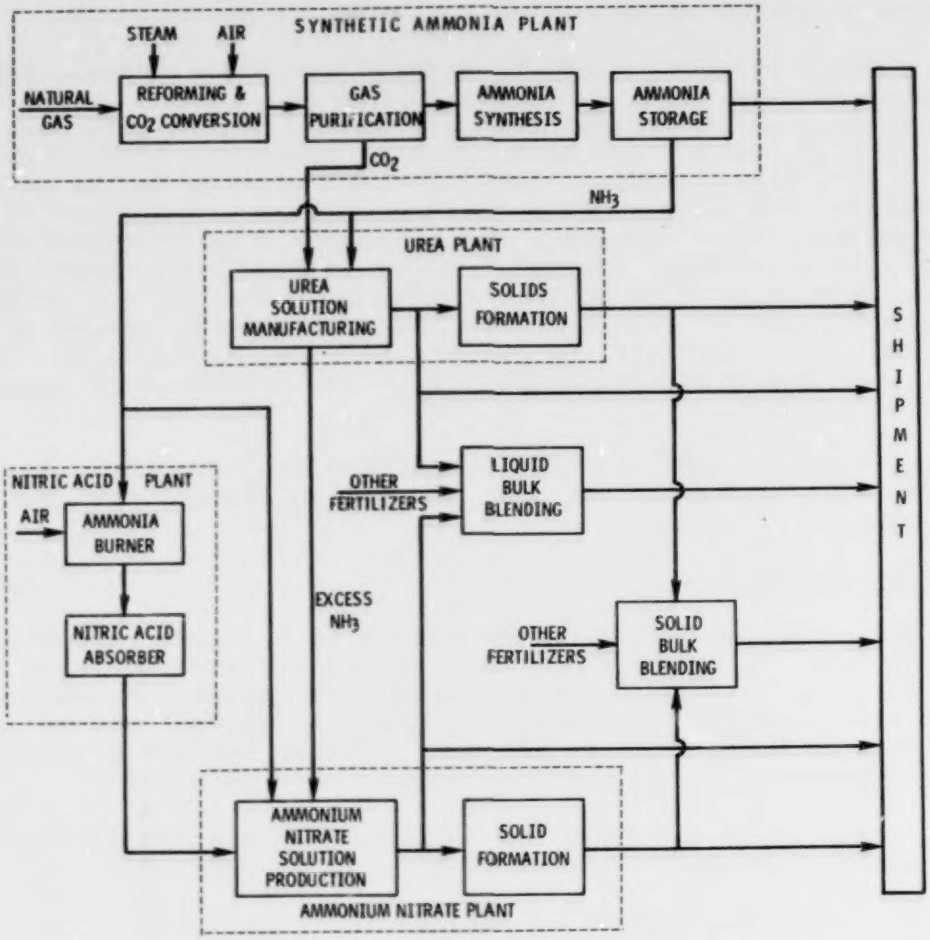
SYNTHETIC AMMONIA PLANT
STEAM
AIR
NATURAL GAS
REFORMING & CO_2 CONVERSION
GAS PURIFICATION
AMMONIA SYNTHESIS
AMMONIA STORAGE
CO_2
NH_3
UREA PLANT
UREA SOLUTION MANUFACTURING
SOLIDS FORMATION
SHIPMENT
LIQUID BULK BLENDING
OTHER FERTILIZERS
NITRIC ACID PLANT
AIR
AMMONIA BURNER
NITRIC ACID ABSORBER
EXCESS NH_3
OTHER FERTILIZERS
SOLID BULK BLENDING
AMMONIUM NITRATE SOLUTION PRODUCTION
SOLID FORMATION
AMMONIUM NITRATE PLANT

Figure 2. Potential interrelationships of various manufacturing lines at a nitrogen fertilizer plant.

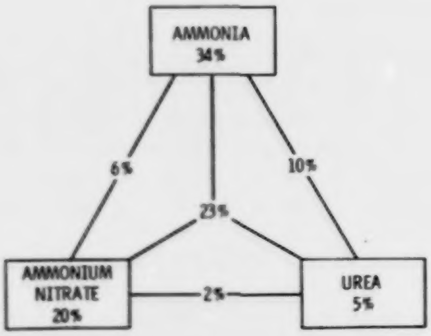
AMMONIA 34%
6%
10%
23%
AMMONIUM NITRATE 20%
2%
UREA 5%

Figure 3. Approximate percentage of nitrogen fertilizer plants having single or specified combinations of manufacturing processes.

COMPONENT PROCESS DESCRIPTIONS

This section presents process descriptions for synthetic ammonia, ammonium nitrate, urea, and nitric acid production. A more extensive discussion of each process, except nitric acid, is available in the air source assessment documents (1-3). An air source assessment document has also been written on the bulk blending of fertilizers (5). This operation can also occur at nitrogen fertilizer plants. Air emissions from this process are readily identifiable. However, water effluent only results from the occasional washing down of trucks and blending equipment. The composition of the resulting stream is highly random and its flow is a small part of the overall plant effluent flow. Therefore, bulk blending of fertilizers is not discussed separately in this document.

A later section, entitled "Effluent Origins," discusses the origin of water effluents for each process in the nitrogen fertilizer plant.

Ammonia Industry

Synthetic ammonia in the United States is produced predominantly (98% of total production) by the catalytic steam reforming of natural gas. In this process hydrogen feedstock for ammonia synthesis is obtained by reacting natural gas with steam. The remaining 2% of production obtains hydrogen feedstock from electrolysis cells in chlorine-caustic soda plants (3).

Six process steps are required to produce synthetic ammonia by the catalytic steam reforming of natural gas method:

1. natural gas desulfurization
2. catalytic steam reforming
3. carbon monixide shift
4. carbon dioxide removal
5. methanation
6. ammonia synthesis

The first, third, fourth, and fifth steps are designed to remove impurities such as sulfur, carbon monoxide (CO), carbon dioxide (CO_2), and water from the feedstock, the hydrogen, and the synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen is introduced into the process. The sixth step produces anhydrous ammonia from the synthesis gas:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (1)$$

---

(5) Rawlings, G. D., and R. B. Reznik. Source Assessment: Fertilizer Mixing Plants. EPA-600/2-76-032c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 187 pp.

While all ammonia plants use this basic process, process details such as pressures, temperatures, and quantities of feedstock vary from plant to plant. A general process flow diagram of a typical synthetic ammonia plant using the catalytic steam reforming process is shown in Figure 4 (3).

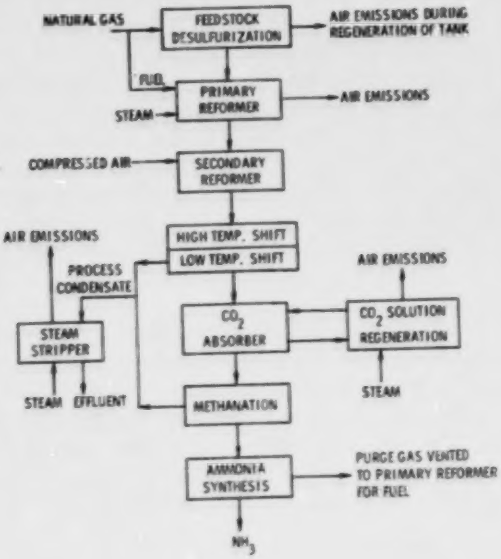
NATURAL GAS
FEEDSTOCK DESULFURIZATION
AIR EMISSIONS DURING REGENERATION OF TANK
FUEL
PRIMARY REFORMER
STEAM
AIR EMISSIONS
COMPRESSED AIR
SECONDARY REFORMER
AIR EMISSIONS
HIGH TEMP. SHIFT
LOW TEMP. SHIFT
PROCESS CONDENSATE
AIR EMISSIONS
STEAM STRIPPER
CO_2 ABSORBER
CO_2 SOLUTION REGENERATION
STEAM
EFFLUENT
STEAM
METHANATION
AMMONIA SYNTHESIS
PURGE GAS VENTED TO PRIMARY REFORMER FOR FUEL
NH_3

Figure 4. General process flow diagram of a typical ammonia plant (3).

Natural Gas Desulfurization--
The sulfur content of natural gas feedstock must be reduced to as low a level as is economically possible to prevent nickel catalyst poisoning in the primary reformer. The total sulfur concentration in pipeline grade natural gas ranges from 229 μg/m³ to 915 μg/m³, with an average value of 450 μg/m³ (3). The concentration in the feedstock must be reduced to less than 280 μg/m³.

Over 95% of the ammonia plants use activated carbon fortified with a metallic additive, such as copper, for feedstock desulfurization. The remainder of the plants use a zinc oxide bed which is replaced instead of being regenerated at the plant. Ammonia plants using activated carbon for desulfurization employ a dual-tank system so that one tank is always onstream while the other is being regenerated.

Catalytic Steam Reforming--
Natural gas leaves the desulfurization tank containing less than 150 μg/m³ sulfur (3). This sweetened natural gas is mixed with process steam and preheated to approximately 540°C in the heat recovery section of the primary reformer. The steam-gas mixture enters the vertically supported primary reformer tubes, which are filled with a nickel-based reforming catalyst. The reforming

reaction (Equation 2) is endothermic and requires a heat input of 227 kJ/mole:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2)$$

Radiant heat for the reforming reaction is normally supplied by firing natural gas and purge gas (from the synthesis loop) on the outside of the reformer tubes. Fuel oil is also used for heating. Approximately 70% of the methane is converted to hydrogen and carbon monoxide in the primary reformer. Process gas is sent to the secondary reformer, where it is mixed with air that has been compressed in a centrifugal compressor to approximately 3.4 MPa and preheated to about 480°C in heat exchangers in the primary reformer. Sufficient air is added to produce a final synthesis gas having a hydrogen-to-nitrogen molar ratio of 3:1.

Carbon Monoxide Shift--
After cooling, the secondary reformer effluent gas (12.0% CO and 8.4% CO_2 on a dry weight basis) enters a high temperature (330°C to 550°C) CO shift converter which is filled with an iron oxide shift catalyst promoted with chromium oxide. Conversion of water and carbon monoxide to carbon dioxide and hydrogen with the addition of steam is necessary for economical use of the raw synthesis gas. The following reaction takes place in the CO shift converter:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

Shift gas is cooled to approximately 200°C in a heat exchanger and passes to the low temperature shift converter for further CO removal. The final shift gas is cooled from approximately 200°C to approximately 55°C and enters the carbon dioxide absorption system. Unreacted steam is condensed and separated from the gas in a knockout drum. This condensed steam is the source of more than 90% of the wastewater generated at a synthetic ammonia plant.

A 544-metric ton/day ammonia plant produces 7.89×10^{-3} m^3/s of condensed steam (process condensate). A 900-metric ton/day plant produces 1.39×10^{-2} m^3/s of condensate. This water contains approximately 600 g/m^3 to 1,200 g/m^3 ammonia, 200 g/m^3 to 2,000 g/m^3 methanol, and 200 g/m^3 to 2,800 g/m^3 carbon dioxide (6-9).

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(6) Quartulli, O. J. Stop Wastes: Reuse Process Condensate. Hydrocarbon Processing, 54(10):94-99, 1975.

(7) Romero, C. J., D. A. Brown, and J. H. Mayes. Treatment of Ammonia Plant Process Condensate Effluent. EPA-600/2-77-200, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1977. 85 pp.

Ammonia in the process condensate is formed in the high temperature shift converter. It is present as ammonium bicarbonate because the condensate is saturated with carbon dioxide. Methanol is formed in the low temperature shift converter. The condensate also contains small amounts (less than 1 g/m^3) of sodium, iron, copper, zinc, calcium, and aluminum, which enter the process stream through contact with catalyst, internal refractory, vessel walls, and piping (6, 10).

Process condensate is sent to a steam stripper to remove volatile gases such as ammonia, methanol, and carbon dioxide. The concentration of these materials in the effluent depends on the pH, the amount of steam used, and the original concentration in the condensate. The ammonia content is generally reduced to 50 g/m^3 or less, the methanol concentration to under 100 g/m^3, and the CO_2 concentration to less than 50 g/m^3 (6, 9). From 96 kg to 240 kg of stripping steam are used per cubic meter of condensate (6). Ion exchange units or molecular sieves are then used to further purify the condensate before recycling it to the boilers. Steam and volatile gases are vented to the atmosphere. Trace metals remaining in the process condensate are removed by the ion exchange unit.

Carbon Dioxide Removal--
The final shift gas contains CO_2 which must be removed. [About 1.22 metric tons (11) of CO_2 are produced per metric ton of ammonia.] The removal of CO_2 depends on its acid-gas character; i.e., its tendency to form carbonic acid in water:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \tag{4}$$

Carbonic acid can be absorbed by solutions of amines, for example:

$$2NH_2CH_2CH_2OH + H_2CO_3 \rightarrow (NH_2CH_2CH_2)_2CO_3 + 2H_2O \tag{5}$$

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(8) Spangler, H. D. Repurification of Process Condensate. In: Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1975. pp. 85-86.

(9) Quartulli, O. J. Review of Methods for Handling Ammonia Plant Process Condensate. In: Proceedings of the Fertilizer Institute Environmental Symposium (New Orleans, Louisiana, January 13-16, 1976), The Fertilizer Institute, Washington, D.C. pp. 25-44.

(10) Fineran, J. A., and P. H. Whelchel. Recovery and Reuse of Aqueous Effluent from a Modern Ammonia Plant. In: Ammonia Plant Safety, Vol. 13, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1971. pp. 29-32.

(11) Strelzoff, S. Choosing the Optimum CO_2-Removal System. Chemical Engineering, 82(19):115-120, 1975.

or by solutions of alkaline salts, such as:

$$K_2CO_3 + H_2CO_3 \rightarrow 2KHCO_3 \qquad (6)$$

to form carbonates. These carbonates decompose into CO_2 and the amine or salt on heating, regenerating the absorption solution. The CO_2 scrubbing systems used in the United States today employ either monoethanolamine or hot potassium carbonate as the scrubbing medium (11, 12).

Methanation--
In commercial practice, all CO_2 absorption methods leave a small amount of CO and CO_2 (usually less than 1.0%) which must be removed because it is a poison to most ammonia synthesis catalysts. Residual CO_2 is removed by catalytic methanation. The reaction is conducted over a nickel catalyst (nickel oxide on alumina) at temperatures of 300°C to 600°C and pressures up to 3 MPa according to the following reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (7)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (8)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (9)$$

The methanation reaction is the reverse of the catalytic steam reforming of methane. Methanation is favored for its lower temperatures and removal of excess water. The final synthesis gas at 38°C and approximately 2.5 MPa has a 3:1 molar ratio of hydrogen to nitrogen and contains less than 1% methane and argon.

Ammonia Synthesis--
The purpose of the ammonia synthesis section is to fix the nitrogen with hydrogen as ammonia in the presence of a catalyst. The arrangement and construction of equipment, the composition of catalysts, and the temperatures and pressures used vary from plant to plant.

The first step in the synthesis process is to compress the synthesis gas from the methanation step. Condensed ammonia is separated from the unconverted synthesis gas in a liquid-vapor separator and sent to a let-down separator. The unconverted gas is compressed and preheated to approximately 180°C before entering the synthesis converter.

Synthesis gas enters the converter and is radially dispersed through the triply promoted iron oxide (Fe_3O_4) synthesis catalyst.

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(12) Green, R. V. Synthetic Nitrogen Products. In: Riegel's Handbook of Industrial Chemistry, Seventh Edition, J. A. Kent, ed. Van Nostrand Reinhold Company, New York, New York, 1974. pp. 75-122.

The exit gas from the converter contains approximately 15% ammonia and approximately 14% inerts. This gas is then cooled from approximately 370°C to about 38°C. The ammonia which condenses is separated in a primary separator. A small portion of the overhead gas is taken as a purge to prevent the buildup of inerts such as argon in the circulating gas system (12). The purge gas is cooled to -23°C in order to condense ammonia and minimize ammonia loss, and is then used as fuel in the primary reformer (13).

Liquid ammonia from the primary, secondary, and purge separators collects in the let-down separator where the ammonia is flashed to 0.1 MPa at -33°C to remove impurities such as argon from the liquid. The flash vapor is condensed in the let-down chiller. Anhydrous ammonia product is drawn from the let-down separator and may be stored in a low temperature (-33°C) atmospheric storage tank or piped to other locations within the plant to produce other products.

Ammonium Nitrate

Ammonium nitrate is produced by an exothermic reaction of ammonia and nitric acid. When a 55% nitric acid feed stream is used, the product of the reaction is an aqueous solution of ammonium nitrate (61%). In practice the heat of reaction (108.8 kJ) may be used to drive off a portion of the water and concentrate the solution to 83% ammonium nitrate. Another major use is to preheat the ammonia and nitric acid feed streams.

In the United States, there are four major solidification processes (see Figure 5) which utilize this basic chemistry to produce solid ammonium nitrate (1). Three of these (prilling, graining, and granulation by spherodization) have the common starting point described above. The fourth, the Stengel process, differs in the method by which the feed reactants are mixed and concentrated as well as in the solid formation method.

These differing processes give the breakdown in final product state shown in Figure 6. This breakdown is based on actual production and indicates that 92% of all solid product is formed by prilling, 7% by granulation, and 1% by graining. Prilling is considered to be the main process and will be discussed further. The remaining three processes are briefly described on page 19.

Prilling Processes--

Ammonium nitrate solution can be solidified in four major processes as mentioned previously. This assessment centers on the

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(13) Haslam, A. A., and W. H. Isalski. Hydrogen from Ammonia Plant Purge Gas. In: Ammonia Plant Safety, Vol. 17, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1975. pp. 80-84.

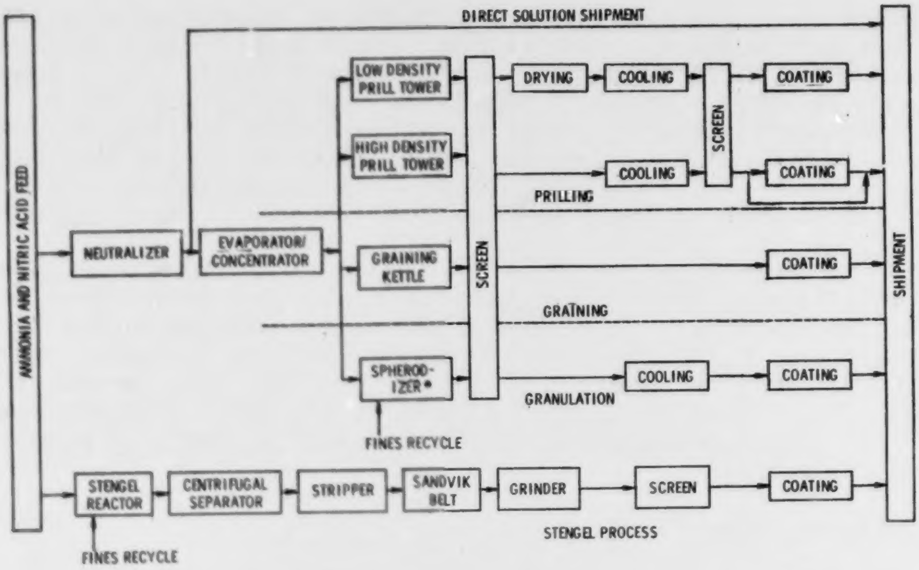
DIRECT SOLUTION SHIPMENT
AMMONIA AND NITRIC ACID FEED
NEUTRALIZER
EVAPORATOR/ CONCENTRATOR
LOW DENSITY PRILL TOWER
HIGH DENSITY PRILL TOWER
GRAINING KETTLE
SPHERODIZER*
SCREEN
DRYING
COOLING
SCREEN
COATING
COOLING
COATING
PRILLING
COATING
GRAINING
COOLING
COATING
GRANULATION
FINES RECYCLE
STENGEL REACTOR
CENTRIFUGAL SEPARATOR
STRIPPER
SANDVIK BELT
GRINDER
SCREEN
COATING
STENGEL PROCESS
FINES RECYCLE
SHIPMENT

Figure 5. Generalized flow sheet of ammonium nitrate production processes.

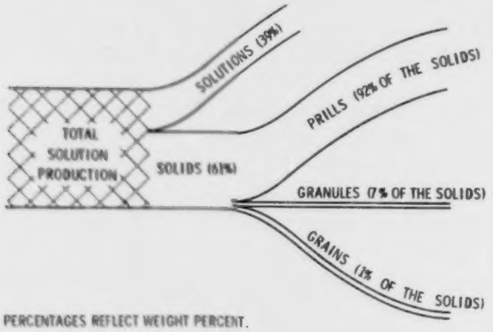

Figure 6. Physical states of ammonium nitrate products.

prilling process, because at least 92% of all solid ammonium nitrate in the United States is produced by this method.

The basic prilling process (14) consists of spraying hot, concentrated ammonium nitrate solution from the top of a tower. In descending countercurrent to a lower temperature airstream, the droplets are formed into spherical particles between 84 μm and 2.38 mm in diameter. This basic procedure is actually only one step of what is termed the prilling process today, which includes the following:

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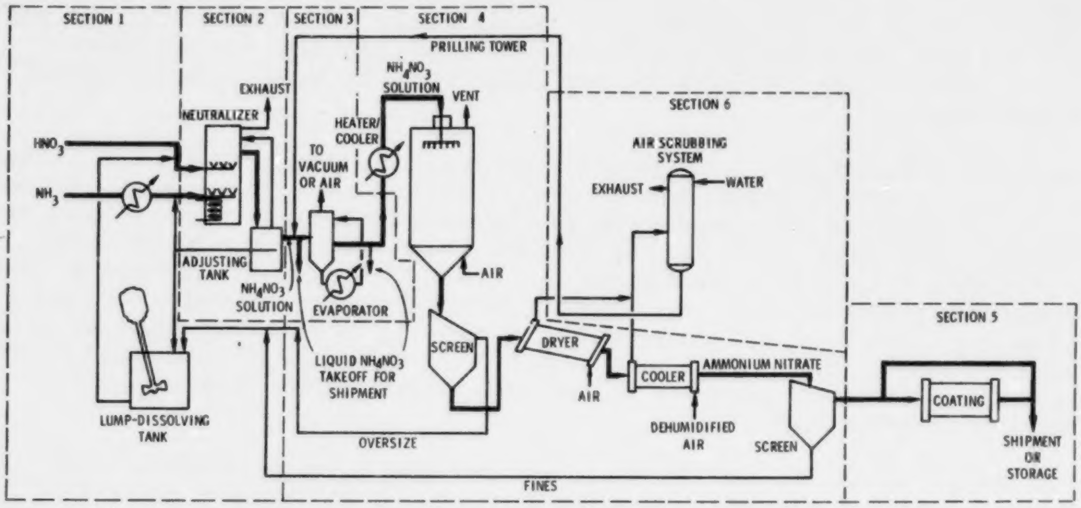
(14) Williams, L., L. F. Wright, and R. Hendricks. Process for the Production of Ammonium Nitrate. U.S. Patent 2,402,192 (to Consolidated Mining and Smelting Co. of Canada, Ltd.), June 18, 1946.

- feed preparation and recycle
- neutralizer and liquid storage
- evaporation/concentration
- particle formation
- product preparation
- dust control

The above areas are distinguished as six sections on the generalized flow sheet in Figure 7 by dashed lines.



SECTION 1
SECTION 2
SECTION 3
SECTION 4
PRILLING TOWER
NH_4NO_3 SOLUTION
VENT
EXHAUST
NEUTRALIZER
HEATER/ COOLER
TO VACUUM OR AIR
HNO_3
NH_3
ADJUSTING TANK
NH_4NO_3 SOLUTION
EVAPORATOR
AIR
SECTION 6
AIR SCRUBBING SYSTEM
EXHAUST
WATER
SCREEN
DRYER
LIQUID NH_4NO_3 TAKEOFF FOR SHIPMENT
LUMP-DISSOLVING TANK
AIR
COOLER
AMMONIUM NITRATE
SECTION 5
COATING
DEHUMIDIFIED AIR
SCREEN
SHIPMENT OR STORAGE
OVERSIZE
FINES

Figure 7. Prilling process flow diagram.

Section 1 in Figure 7 contains the feed pretreatment and the recycle loops entering the main process stream before the neutralizer. Ammonia is heated to vaporization (approximately 66°C to 77°C) before being introduced under a liquid nitric acid head. The nitric acid is heated in 85% of the plants to approximately 82°C.

A lump dissolving tank dissolves the over- and undersize material recovered from the screening process. The material is then recycled to the process as a weak (approximately 60% ammonium nitrate) liquor.

Section 2 of Figure 7 contains the neutralizer and an adjusting tank. The neutralizer is a vertical, cylindrical vessel in which the reaction between ammonia and nitric acid takes place. A hydrostatic head of ammonium nitrate is maintained by judicious placement of the overflow pipe. The reaction takes place under this head.

As a result of the highly exothermic reaction and the water content of the nitric acid feed, a steam exhaust exists. This stream may be used to preheat the ammonia and/or it may be exhausted to the atmosphere or condensed.

The adjusting tank is used to store the 83% ammonium nitrate solution from the neutralizer, to receive overflow from a head tank on the prilling tower, and to supply the evaporator/concentrator on a demand basis. The actual ammonium nitrate concentration in such tanks may therefore range from 81% to 83%.

Section 3 in Figure 7 consists of the evaporator/concentrator. This portion of the process is responsible for concentrating the 81% to 83% solution to a 95% to 96% solution for low density prill production or to a 99.5+% solution for high density prill production.

Section 4 in Figure 7 includes the prilling tower, various sizing screens, and the dryer and cooler. In the prilling tower, ammonium nitrate is received from the evaporator/concentrator and contained in a head tank at the top of the tower. The head tank maintains a constant pressure on a spray device which sprays the ammonium nitrate into the tower. Droplets are formed and fall countercurrent to a rising airstream. The airstream acts as a heat transfer mechanism that cools the ammonium nitrate below its melting point and permits solidification of the droplet into a spherical particle.

Two solid products can be made by the prilling process: low density prills and high density prills. For the low density prills, a 95% to 96% solution is used. As these droplets descend in the tower, the prill cools, trapping the water. When the prill is dried, the void space left results in a low density prill with a bulk density of 770 kg/m^3. Approximately 40% of all prilled ammonium nitrate is low density. Because high density prilling utilizes a more concentrated ammonium nitrate solution, the resulting voids are fewer and a prill with bulk density of 860 kg/m^3 results.

After solidifying, prills are screened to remove oversize and undersize material. Low density prills then go to a two-stage drying process to drive off excess water, followed by cooling and additional screening. High density prills do not require the drying step and go directly to cooling followed by screening.

Low density prills which are not used as an onsite intermediate (e.g., in explosive manufacturing or fertilizer mixing) are coated with diatomaceous earth or other material as a water barrier. High density prills are generally not coated (approximately 3% are coated); instead they are made with an additive that enhances shelf life.

The final product may be stored in warehouses (for a short period of time), shipped in bulk in railroad cars or bulk trucks, or bagged in 23-kg or 45-kg quantities.

Other Processes--

Three processes other than prilling were identified in Figure 5. The basic differences in the products are crystal structure and particle strength.

The graining process employs feed streams and a neutralizer similar to those used in the prilling process. The stream then goes through an evaporation step to produce a 98% ammonium nitrate solution. This stream is discharged to graining kettles where the mix is stirred by large plows until it cools.

The SPHERODIZER® granulation process, developed by C&I Girdler Inc. (15-17), utilizes a neutralizer and evaporator/concentrator as described previously. The method by which the solids are formed, however, differs greatly. The 99.5% ammonium nitrate is sprayed through nozzles into a rolling bed of particles in the rotating granulation drum (18). A dam in the drum retains the particles a sufficient length of time to permit several layers to build up on each granule. The granules then pass over the dam into the cooling section where they are screened and cooled; then they are coated and bagged.

The Stengel process uses the special reactor shown in Figure 8 (19, 20). Preheated nitric acid and ammonia are continuously fed to the reactor. The heat of reaction vaporizes the water in the nitric acid feed. A solution of 98% ammonium nitrate and trace ammonia flows from the reactor to a centrifugal separator which removes the ammonium nitrate and runs it through an air stripper that reduces the moisture content to approximately 0.2%.

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(15) Smith, B. G. Process for Production of Fertilizer Pellets. U.S. Patent 2,926,079 (to C&I Girdler Inc.), February 23, 1970.

(16) Tyler, F. J., and T. D. Striggles. Process for Pelletizing a Water Soluble Material. U.S. Patent 3,227,789 (to C&I Girdler Inc.), January 4, 1966.

(17) Tyler, F. J., and T. D. Striggles. Apparatus for Making Spherical Pellets of Water Soluble Substances. U.S. Patent 3,333,297 (to C&I Girdler Inc.), August 1, 1967.

(18) Reed, R. M., and J. C. Reynolds. The Spherodizer Granulation Process. Chemical Engineering Progress, 99(2):62-66, 1976.

(19) Hester, A. S., J. J. Dorsey, Jr., and J. T. Kaufman. Stengel Process Ammonium Nitrate. Industrial and Engineering Chemistry, 46(4):622-632, 1954.

(20) Stengel, L. A. Process for Producing Ammonium Nitrate. U.S. Patent 2,568,901 (to Commercial Solvents Corp.), September 25, 1951.

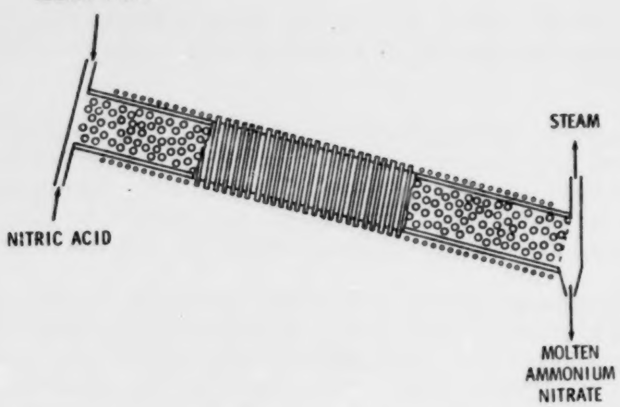


Figure 8. Stengel reactor (20).

The molten ammonium nitrate flows into a weir box for distribution onto an endless, stainless steel, water-cooled (Sandvik) belt. Solid ammonium nitrate is removed from the belt by a doctor blade. This material is fed to grinders, then screened, coated, and bagged. The oversize material is recycled to the grinder and the fines are returned to the process. Particle formation may also be accomplished using a prill tower, as described previously.

Urea Manufacture

Urea [$CO(NH_2)_2$] is produced by the reaction of ammonia and carbon dioxide to form ammonium carbamate ($NH_2CO_2NH_4$) which is then dehydrated to form urea and water. There are over 15 production methods by which this reaction is carried out. All processes, however, follow the basic scheme shown in Figure 9 (2). The reaction of liquid ammonia and carbon dioxide gas takes place at approximately 175°C to 200°C and 19.2 MPa to 23.2 MPa. The ammonium carbamate formed is dehydrated to form urea. The resulting urea stream goes to various solution concentration, solidification, and packaging steps before leaving the plant.

Solution Production--

While process chemistry remains constant, there are variations in vessel design, operating conditions, and type and quantity of unreacted material recycle. These variations result in three major classes of urea processes (for solution formation), based on the type or quantity of recycle: once-through processes, partial recycle processes, and total recycle processes.

In once-through processes, there is no recycle of unreacted material. The reactants enter the reactor, achieve 40% to 45% conversion to urea, and then proceed to a decomposer. Here unreacted carbamate is decomposed to ammonia and carbon dioxide

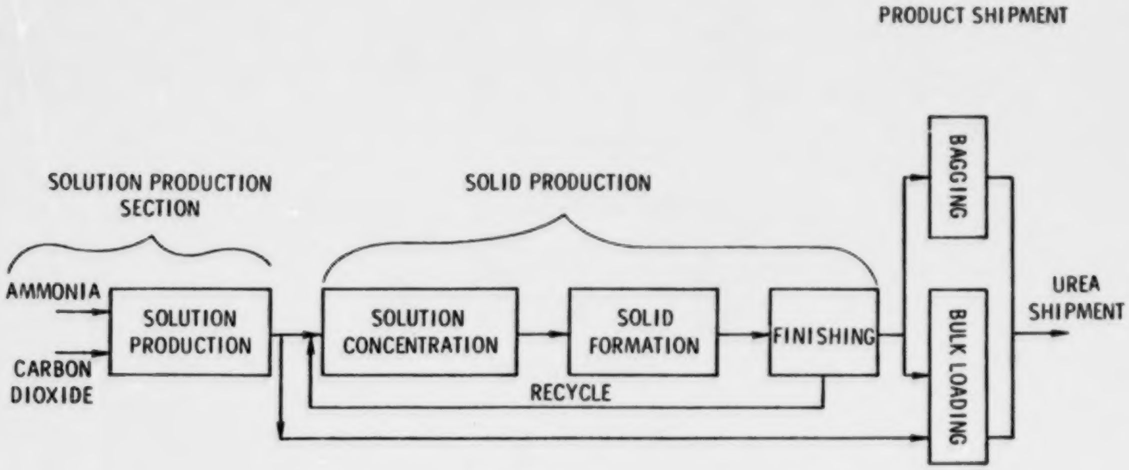

PRODUCT SHIPMENT
SOLUTION PRODUCTION SECTION
SOLID PRODUCTION
AMMONIA
CARBON DIOXIDE
SOLUTION PRODUCTION
SOLUTION CONCENTRATION
SOLID FORMATION
FINISHING
RECYCLE
BAGGING
BULK LOADING
UREA SHIPMENT

Figure 9. Block diagram of urea production process.

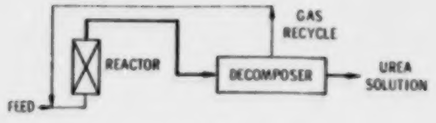
which is then separated from the urea and water. The aqueous urea goes for further processing. The mixed gas stream goes directly to another fertilizer manufacturing facility as a feed stream.

In the partial recycle process, the reactants are fed to the reactor with approximately 200% excess ammonia versus the 2:1 to 3:1 ammonia-to-carbon dioxide molar ratio in the once-through process. This excess has been shown to give a urea equilibrium yield of at least 80%. Before going to a decomposer and proceeding as described above, the reactor effluent passes through an excess ammonia separator. The ammonia recovered is recycled to the reactor.

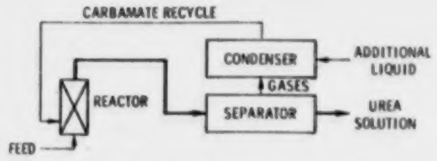
Figure 10 is an extreme simplification of the basic process differences in the three total recycle systems available from various contractors (2). Each recycles all unreacted material to the reactor. In the gas recycle system, the reactor effluent is decomposed in the manner described for the once-through process. The decomposed gases are then separated and recycled. In the liquid recycle system, the separated carbamate solution is recycled to the reactor. In the gas/liquid recycle system, ammonia is recycled basically as a gas and carbon dioxide (with a stoichiometric amount of ammonia) is recycled as a carbamate slurry.

Solid Urea Production--

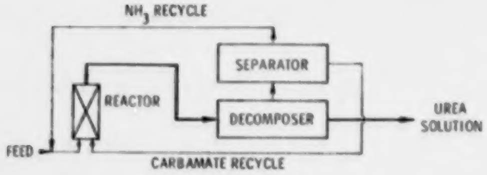
Figure 11 is a flowsheet of the entire urea solidification process (2). The formation of solid urea requires a critical balance between temperature, retention time, and airflow due to several physical characteristics: melting point, heat of crystallization, and decomposition properties. These factors lead to careful


GAS
RECYCLE
REACTOR
DECOMPOSER
UREA
SOLUTION
FEED

A. Basic gas recycle process


CARBAMATE RECYCLE
CONDENSER
ADDITIONAL
LIQUID
GASES
REACTOR
SEPARATOR
UREA
SOLUTION
FEED

B. Basic liquid recycle process


NH_3 RECYCLE
SEPARATOR
REACTOR
DECOMPOSER
UREA
SOLUTION
FEED
CARBAMATE RECYCLE

C. Basic gas / liquid recycle process

— PRODUCT-CONTAINING STREAMS
— RECYCLE, FEED, OR OTHER ANCILLARY STREAMS

Figure 10. Total recycle urea processes.

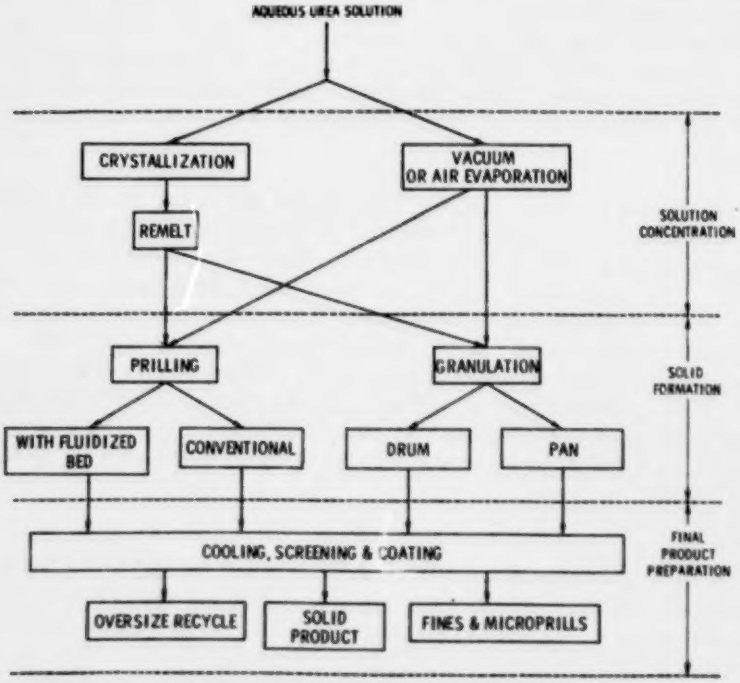

AQUEOUS UREA SOLUTION
CRYSTALLIZATION
VACUUM
OR AIR EVAPORATION
REMELT
SOLUTION
CONCENTRATION
PRILLING
GRANULATION
SOLID
FORMATION
WITH FLUIDIZED
BED
CONVENTIONAL
DRUM
PAN
COOLING, SCREENING & COATING
FINAL
PRODUCT
PREPARATION
OVERSIZE RECYCLE
SOLID
PRODUCT
FINES & MICROPRILLS

Figure 11. Solidification of urea (2).

control and at times adaptation of established techniques depending upon the environment in which the material is produced.

Solution concentration is achieved by either a crystallizer or evaporator. The purpose of both is to achieve a more concentrated stream while maintaining a low biuret ($H_2NCONHCONH_2$) content (a contaminant that can result from heat exposure). When a crystallizer is used, the crystals must be dried and melted before going to solid formation. Water effluents result from these operations directly from crystallization, and from off-gas condensation in evaporators.

Solid product can be formed by two methods, prilling and granulation. The Spherodizer granulation process accounts for approximately 85% of all the solid urea that is produced domestically. In this process, urea melt enters a granulation drum through a spray bar which distributes the melt on a tumbling bed of particles. Particles of appropriate diameter exit the drum by passing over a retaining dam and go through a cooling section.

The second method of solid formation is prilling. In this process, concentrated urea solution is pumped to the top of a tower 30.5 m to 33.5 m high and forced through a spray device in a method similar to that previously described for ammonium nitrate.

Final product preparation may include cooling of the material, screening of the final product, coating for preservation purposes, and possibly bagging.

Nitric Acid Production

In the United States, nitric acid is manufactured commercially by the ammonia oxidation process. A series of three reactions is required to convert ammonia, the feed substance, to nitric acid. In the first reaction, ammonia is oxidized to either NO or N_2 in the presence of oxygen (O_2) and a platinum catalyst as follows:

$$4H_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (10)$$

or

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (11)$$

Both reactions are rapid, complete, and highly exothermic (ΔH equals -226 kJ/mole and -317 kJ/mole, respectively), with higher operating temperatures and gas velocities favoring higher yields of NO, the desired product. Operating pressure has some effect on yield, and this fact is exploited in the dual pressure process. Industrial experience has shown that a 96% yield of NO can be expected at 800 kPa and 900°C while a yield of 98% can be expected at atmospheric pressure (100 kPa) and 850°C (21).

In the second reaction, NO and O_2 react slowly, compared to the first pair of reactions, to yield nitrogen dioxide by the following exothermic (ΔH equals -114 kJ/mole) reaction:

$$2NO + O_2 \rightleftarrows 2NO_2 \tag{12}$$

Lower temperature and higher pressure favor the formation of NO_2. An equilibrium is achieved between NO_2 and nitrogen tetraoxide (N_2O_4) in the following exothermic reaction:

$$2NO_2 \rightleftarrows N_2O_4 \tag{13}$$

In this case lower temperatures and higher pressures favor the formation of N_2O_4 (21).

In the third reaction, nitrogen dioxide combines with water to form nitric acid as follows:

$$3NO_2(g) + H_2O(\ell) \rightleftarrows 2HNO_3(aq) + NO(g) \tag{14}$$

This reaction is also exothermic (ΔH equals -136 kJ/mole), and lower temperature and higher operating pressure favor the formation of $HNO_3(aq)$.

In practice, operating gage pressures of the ammonia oxidation process fall within three ranges: atmospheric (0 kPa to 70 kPa), intermediate (140 kPa to 410 kPa), and high pressure (550 kPa to 830 kPa). As noted, higher pressures are advantageous to the formation of the desired products in reactions 12 and 14. Therefore 91% of the nitric acid produced in the United States is produced within the high pressure range of operating pressures (22). A typical process flowsheet common to a high pressure system is presented in Figure 12 (23).

In the dual pressure process, which is more common in Europe than in the United States, advantage is taken of the conversion of

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(21) Strelzoff, S., and D. J. Newman. Nitric Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 13. John Wiley & Sons, Inc., New York, New York, 1967. pp. 796-814.

(22) Spencer, E. F., Jr. Pollution Control in the Chemical Industry. In: Industrial Pollution Control Handbook, H. F. Lund, ed. McGraw-Hill, Inc., New York, New York, 1971. pp. 14-4 to 14-6.

(23) Mandelik, B. G., and W. Turner. Selective Oxidation in Sulfuric and Nitric Acid Plants: Current Practices. Chemical Engineering, 84(9):127-130, 1977.

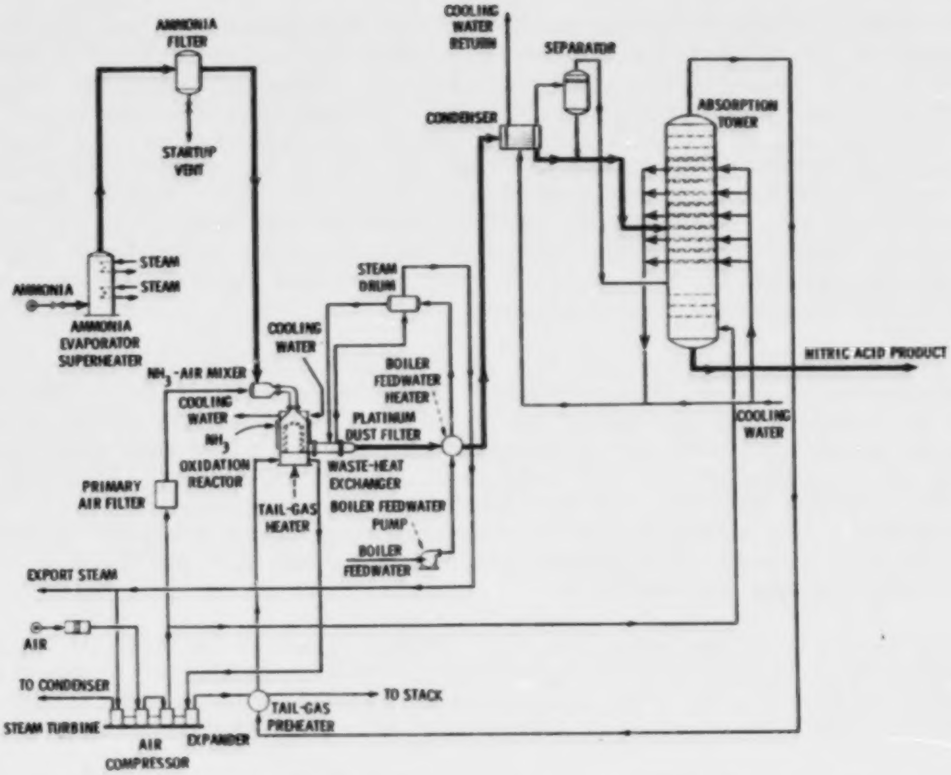
AMMONIA FILTER
STARTUP VENT
COOLING WATER RETURN
SEPARATOR
CONDENSER
ABSORPTION TOWER
STEAM
STEAM
AMMONIA
AMMONIA EVAPORATOR SUPERHEATER
STEAM DRUM
COOLING WATER
NITRIC ACID PRODUCT
NH_3-AIR MIXER
BOILER FEEDWATER HEATER
COOLING WATER
NH_3
PLATINUM DUST FILTER
COOLING WATER
OXIDATION REACTOR
WASTE-HEAT EXCHANGER
PRIMARY AIR FILTER
TAIL-GAS HEATER
BOILER FEEDWATER PUMP
BOILER FEEDWATER
EXPORT STEAM
AIR
TO CONDENSER
TO STACK
TAIL-GAS PREHEATER
STEAM TURBINE
AIR COMPRESSOR
EXPANDER

Figure 12. Typical pressure system flowsheet (23).

NH_3 to NO (Reaction 10) at lower pressures. This process utilizes low pressure ammonia oxidation followed by high pressure absorption of NO_2 in water.

In all of the processes ammonia is first vaporized by steam, then mixed with excess compressed air. This mixture is passed through the platinum catalyst (which may also contain less than or equal to 10% rhodium to increase catalyst strength) in the ammonia oxidation reactor. An operating temperature of approximately 900°C is typically used (23). As mentioned earlier, 95% to 98% of the feed NH_3 is converted to NO (21, 23).

Temperature in the reactor is controlled by cooling water that circulates through the reactor shell. Some cooling occurs when tail gas is circulated through the heater below the reactor as shown in Figure 12.

The gas containing NO is cooled following the ammonia oxidation reactor. As shown in Figure 12, the heat can be recovered to produce steam which can be used for various purposes including 1) powering the air compressor drive turbine, 2) vaporizing the ammonia at the head end of the process, and 3) exporting for use in other processes in the fertilizer plant.

Additional cooling takes place in the condenser. The steam condenses to form weak nitric acid. This liquid fraction enters the side of the absorption tower while the gaseous fraction enters the bottom. The two fractions flow countercurrent in the tower. Cooling water or liquid ammonia are also applied to the tower to lower and control the temperature of the exothermic reactions and to induce additional condensation of the steam. Additional "bleacher" air is supplied to the absorption tower to ensure more complete formation of NO_2 from NO originating both from incomplete oxidation prior to the absorption tower and formation as a byproduct of the absorption reaction.

Tail gas exits the top of the absorption tower, and typically contains 0.2% to 0.3% nitrogen oxides by volume (21). The gas can be circulated as shown in Figure 12 to provide cooling and to supply power to the air compressor by means of a gas expander. Tail gas treatment can be achieved by various catalytic systems which convert the NO_x to NO which can be discharged (24). Other processes, for example, extended absorption or caustic scrubbing result in cleaner off-gases because they do not produce a stream with NO_x in the exhaust.

Concentration processes are not normally used in nitric acid production for fertilizer manufacture. The fertilizer industry uses dilute acid (55% to 65%) which can typically be produced by the ammonia oxidation process discussed above without concentration.

Energy recovery from the exothermic reactions as discussed above provides sufficient energy so that some nitric acid plants can operate without auxiliary power (21).

EFFLUENT ORIGINS

Two basic effluent source types exist in a nitrogen fertilizer plant--point and nonpoint. Point sources are those which originate as a definite wastewater stream from a particular process. Nonpoint sources originate from random leaks or from large areas within a plant. In the following sections, point sources for each of the four basic processes will be discussed, followed by a general discussion of nonpoint sources for the entire plant.

Point Sources

Ammonia--

Effluent from the production of ammonia can result from condensate from the steam stripper exhaust or from spent regenerant used in the ion exchange purification of the recycled condensate. Condensate must be purified to remove ammonia and other ions before it can be used as boiler feedwater.

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(24) Chemical Week, 98(8):85, 1966.

Ammonium Nitrate--
Point sources of wastewater in the ammonium nitrate manufacturing process may include condensate from the neutralizer and the evaporator exhausts and solutions from air pollution control equipment used on the cooler and/or dryer. Less than 50% of the ammonium nitrate plants condense the exhausts from the neutralizer and evaporator. It is estimated that over one-half of these plants either recycle the material or sell/use it as a dilute fertilizer solution. Thus less than an estimated 25% of the ammonium nitrate plants release process condensate to a receiving body or send it into a treatment unit. Effluent from air pollution control equipment may be blended into fertilizer solutions where markets exist.

Urea--
Point sources in the manufacture of urea are condensate of the evaporator exhaust and filtrate from the concentration of urea solution when a crystallizer is used. Plants using a vacuum evaporator (∿50%) condense the exhaust so that they can recover the nitrogen value in the stream as a dilute fertilizer (1). When airswept evaporators are used the exhaust is scrubbed and vented to the atmosphere, and the scrubbing liquid may be recovered as a dilute fertilizer solution. Less than 25% of the plants use crystallizers (1).

Nitric Acid--
In general there are no point sources of water effluent from the actual nitric acid manufacturing line (25). There may be effluent from the cooling towers or spills, and these are covered in the following sections.

Cooling Towers--
Manufacture of ammonia, urea, and nitric acid requires a cooling system for temperature control during certain processing steps. Closed loop cooling towers are generally used, although older plants may still use once-through or single-pass cooling towers. The designs of these cooling towers are the same as those of towers used in other industrial operations.

Closed loop cooling systems require a periodic tower blowdown. This blowdown is discharged to a receiving body or to a treatment system. Although the cooling system is a noncontact process, the blowdown (or discharge in the case of a single-pass system) may still contain NH_3 or nitrate (NO_3) from two sources. The first of these is absorption of ammonia from the ambient air (25).

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(25) Train, R. E., A. Cywin, E. E. Martin, and R. Strelow. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Chemicals Segment of the Fertilizer Manufacturing Point Source Category. EPA-440/1-74-011-a, U.S. Environmental Protection Agency, Washington, D.C., March 1974 168 pp.

This complication is especially acute at a nitrogen fertilizer plant considering the elevated (compared with other ambient levels) levels of ammonia present. Rainfall in open areas (i.e., farmland) has been shown to contain as much as 1.6 ± 0.5 g/m^3 NH_3 (26), and the levels that can be achieved from ambient pickup at a nitrogen fertilizer plant may be significant. Ammonia will also be converted to nitrate as a result of bacterial action especially in hot weather.

A second source of NH_3 or NO_3 is small leaks into the cooling system from process streams. Even slight leaks may lead to appreciable concentrations of NH_3 or NO_3 in the cooling water. Such a source occurs in the inlet hot gas line on the nitric acid plant where flashing causes extreme corrosion. This corrosion results in leaks to the cooling system.

Other potential pollutants are any inhibitors added to the cooling tower water to prevent corrosion (27). Chemicals such as copper, chromium, or zinc compounds will definitely show up in any blowdown in minute amounts. Other compounds used for boiler feedwater treatment can also appear in the cooling water if the boiler blows down to the cooling tower.

Nonpoint Sources

In nitrogen fertilizer plants, there are various nonpoint sources that can contribute a major portion of the water effluent.

Leaks and Spills--

In any plant, a certain number of valve and pump leaks as well as random spills can be expected. In the nitrogen fertilizer plant, these leaks can become a major contributor due to the sometimes corrosive character of the material (25). For example, the carbamate recycle is a highly corrosive slurry, and pump seals on such recycle lines must be replaced frequently. Spills also often occur at shipping facilities.

Plant and Equipment Cleanup--

Spills are often not cleaned up until there is a general plant cleanup, unless they are large enough to require immediate attention. These spills generally occur around loading operations and are hosed down periodically.

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(26) Taylor, A. W., W. D. Edwards, and E. C. Simpson. Nutrients in Stream Draining Woodland and Farmland near Coshocton, Ohio. Water Resources Research, 7(1):81-89, 1971.

(27) Patton, T. H., Jr., W. C. Wood, and R. C. Chopra. Development of a Water Management Plan for an Acid Manufacturing Plant. In: Proceedings of the 28th Industrial Waste Conference, Purdue University, Lafayette, Indiana, 1973. pp. 1032-1046.

Equipment cleanup generally involves the flushing of railroad cars or trucks. This normally occurs in a specified area with proper drainage designed specifically for this use.

Other cleanup sources may result when process vessels must be evacuated and flushed for maintenance and personnel entry.

Additive Filter Cake Back Wash--

The use of additives in the manufacture of high density ammonium nitrate requires filtration to remove raw material insolubles. Periodic renewal of the filter cake results in back washing entrapped nitrate solutions to the sewer.

Runoff--

Rainfall runoff from a plant can be a significant contributor to a plant's total nitrogen loading because it collects ammonia and nitrate from the air and washes down the ground and buildings on which solid fertilizer material may have settled (25).

SECTION 4

EFFLUENT PARAMETERS

As discussed in Section 3, wastewater from the manufacture of nitrogen fertilizer materials originates from many point and non-point sources. The quality and characteristics of a given plant effluent are dependent on the types of processes present at the complex, plant to plant variations in process design and operation, equipment age, level of maintenance, plant drainage and collection, and wastewater treatment methods. These varying parameters cause the effluents from nitrogen fertilizer plants to vary significantly from plant to plant. As a result, it is difficult to define average effluent parameters that are truly representative of the industry as a whole. The approach that has been taken in this study is to present the range encountered for the parameters of concern as well as average values.

EFFLUENT CHARACTERIZATION

Three basic nitrogen pollutant materials occur in wastewater from nitrogen fertilizer production: ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3^--N), and organic nitrogen (ORG-N). Ammonia nitrogen (NH_3-N) can exist in either the un-ionized (NH_3°-N) or ionized (NH_4^+-N) form depending upon the pH and temperature of the wastewater. These two forms of ammonia will be treated as separate species in Section 4. In addition, contaminants other than nitrogen compounds may be present for a particular unit process. In the sections following, effluent parameters for each basic process will be discussed.

Synthetic Ammonia Production

Effluent from the manufacture of ammonia arises when the ammonia synthesis gas is cooled following the low temperature shift conversion. As discussed in the process description, the resulting condensate is routinely steam stripped because EPA regulations require the industry to reduce ammonia discharged in the water. The water stream exiting the condensate stripper is suitable for discharge or recycle as boiler feed water for low pressure boilers.

Typical concentrations of potential pollutants in the steam stripper condensate stream are ≤ 50 g/m^3 ammonia, ≤ 100 g/m^3 methanol, ≤ 50 g/m^3 carbon dioxide, and minor concentrations of metals

(6, 9). Actual concentrations vary from unit to unit depending on the steam stripper operating parameters (e.g., initial pollutant levels, pH, and amount of steam used for stripping). A 544-metric ton/day ammonia plant produces about 7.9 x 10^{-3} m^3/s of steam stripper condensate. Source test data concerning emissions from the condensate steam stripper are reported in a recent study by Gulf South Research Institute in which the authors evaluated different techniques for handling steam stripper overheads at a typical ammonia plant (7). Complete material balances were calculated around a 10-m-tall steam stripper at a 900-metric ton/day ammonia plant generating 1.26 x 10^{-2} m^3/s of process condensate. The condensate stripper system is shown in Figure 13.

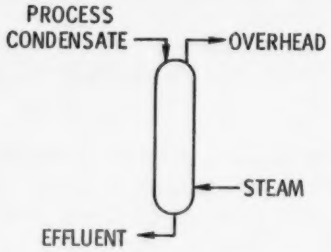

Figure 13. Process condensate steam stripper.

In order to calculate ammonia and methanol effluent factors, a total of 65 individual source test measurements from Reference 7 were used. The average material balance is shown in Table 4.

TABLE 4. MASS BALANCE AROUND THE CONDENSATE STEAM STRIPPER--RESULT OF 65 TEST MEASUREMENTS (7) (kg/hr)

Stream	Stream flow rates	Mass flow rate Ammonia	Mass flow rate Methanol
Process condensate	80,500	39.2	21.1
Steam	7,980	0	0
Overhead	8,680	41.2	22.7
Effluent	81,200	0.57	0.28

Note.—Mass entering the stripper does not exactly equal mass exiting since these values are the averages from 65 test measurements.

Effluent factors for ammonia and methanol from this 900-metric ton/day ammonia plant are shown in Table 5. Average effluent concentrations were 7 g/m^3 for ammonia and 3.4 g/m^3 for methanol, indicating high removal efficiencies for this stripper. Less efficient strippers could have final effluent concentrations and effluent factors higher by up to a factor of ten.

TABLE 5. EFFLUENT DISCHARGE FACTORS FOR A CONDENSATE STEAM STRIPPER (7)
(mg/kg)

Effluent species	Effluent discharge factor
Ammonia	15 ± 105%
Methanol	7.5 ± 97%

Note.—Uncertainty values were calculated using the "Student t" test for 95% confidence limits.

Concentrations of trace metals in the process condensate, stripper overheads, and stripper effluents were measured at six ammonia plants (7). Results of the analyses are presented in Table 6. For companies 100 and 200, metals were analyzed by flame atomic absorption spectrophotometry, while samples from companies 400, 500, 600, and 700 were analyzed by graphite furnace atomic absorption spectrophotometry.

TABLE 6 TRACE METAL CONCENTRATIONS IN PROCESS CONDENSATE (7)
(g/m^3)

Company No.	Metal concentration				
	Chromium	Copper	Iron	Nickel	Zinc
100	<0.5	<0.5	<0.3	<0.5	1.5
200	<0.5	<0.5	<0.3	<0.5	<0.1
400	<0.2	<0.02	<0.1	<0.2	<0.02
500	<0.2	<0.02	<0.1	<0.2	<0.02
600	<0.2	<0.02	<0.1	<0.2	<0.02
700	<0.2	0.045	<0.1	<0.2	<0.02
Average	<0.3	<0.2	<0.2	<0.3	<0.3

Trace metals are carried out of the steam stripper with the effluent. Using the average metals concentration values in Table 6, the average effluent flow rate of 81,200 kg/hr from the 65 source test measurements in Reference 7, and a production rate of 900 metric tons/day, trace metal effluent factors were calculated and are presented in Table 7.

TABLE 7. TRACE METAL EFFLUENT DISCHARGE FACTORS FROM A CONDENSATE STEAM STRIPPER (7)

Metal	Average concentration, g/m^3	Effluent discharge factor, g/kg
Chromium	<0.3	$<6 \times 10^{-5}$
Copper	<0.2	$<4 \times 10^{-5}$
Iron	<0.2	$<4 \times 10^{-5}$
Nickel	<0.3	$<6 \times 10^{-5}$
Zinc	<0.3	$<6 \times 10^{-5}$

Effluent factors in Tables 5 and 7 are characteristic of steam stripper condensate discharged directly to a receiving stream. If condensate is recycled, the only effluent arises when the deionization unit used to further purify the condensate is regenerated. In such a case, the metal concentrations and short-term effluent factors will be higher, but material balance considerations show that long-term effluent factors can be no higher than in the case of direct discharge.

Ammonium Nitrate

Effluent data reported to the Effluent Guidelines Division of the EPA by the nitrogen fertilizer industry were used as a basis for setting effluent standards.[a] These data are compiled and evaluated in Appendix B. Industry data were supplied for ammonium nitrate plants, urea plants, and plants manufacturing ammonium nitrate and urea. Separate data were not reported for effluents from ammonia and nitric acid production because these processes were treated as part of ammonium nitrate and urea production. Effluent from the ammonium nitrate process contained any wastewater from associated ammonia and nitric acid operations.

Ammonia nitrogen and nitrate nitrogen were found to be the basic constituents of the wastewater stream from an ammonium nitrate facility. Average effluent parameters are given in Table 8. The methodology used in deriving these averages is presented in Appendix B. In cases where sampling measurements were taken on a combined ammonium nitrate/urea plant outfall, a proportioning method was used to arrive at ammonium nitrate effluent factors.

Three ammonium nitrate plants also reported organic nitrogen in their wastewater at levels of 8.9 g/m^3, 14.2 g/m^3, and 69.9 g/m^3. This could result from some monoethanolamine from the ammonia unit or from crossover from the urea plant (all three plants make ammonium nitrate, ammonia, and urea). Under normal circumstances, organic nitrogen would not be expected in ammonium nitrate wastewater.

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[a] Data on file at the Effluent Guidelines Division, U.S. Environmental Protection Agency, Washington, D.C., 1977.

TABLE 8. AVERAGE EFFLUENT PARAMETERS FOR NITROGEN FERTILIZER PLANTS

Parameter	Ammonium nitrate[a]	Urea[b]
Wastewater effluent flow rate, m^3/s	0.0327	0.0399
Effluent factor, g/kg:		
NH_3-N	0.862	0.756
NO_3^--N	0.471	0
ORG-N	0	0.275
Effluent concentration, g/m^3:		
NH_3-N	482	120
NO_3^--N	121	0
ORG-N	0	90

[a] An average plant produces 386 metric tons/day of ammonium nitrate.

[b] An average plant produces 342 metric tons/day of urea.

Urea

Ammonia nitrogen and organic nitrogen were found to be the basic constituents of the wastewater stream from a urea facility. Their average effluent factors are derived in Appendix B and shown in Table 8. As in the case of ammonium nitrate, some plants reported data for a combined plant outfall. A proportioning method, described in Appendix B, was used to calculate urea effluent factors.

Three urea plants reported nitrate nitrogen in their wastewater at levels of 6.3 g/m^3, 6.9 g/m^3, and 23.6 g/m^3. This is probably caused by crossover in the drainage systems or by drift of ammonium nitrate material in the air into the urea drainage system, since all three plants also produced ammonium nitrate. Nitrate could also result from the conversion of ammonia or urea to nitrate by biological action, but it was not reported by any plant manufacturing only urea.

Nitric Acid

Effluent data are not available for wastewater originating solely from a modern nitric acid plant with a recirculating cooling system. Aggregated data are reported in the section on ammonium nitrate effluents. Values of effluent parameters for two nitric acid plants equipped with single-pass cooling systems are presented in Table 9 (28, 29). These data are not typical of the industry where the only point source effluent from nitric acid production is cooling tower blowdown.

TABLE 9. EFFLUENT FROM NITRIC ACID PLANTS WITH SINGLE-PASS COOLING SYSTEMS

Parameter	Plant A	Plant B
Production, metric tons/day (100% HNO_3)	180	51
Effluent concentration, g/m^3:		
NH_3-N	0.03	0.3
NO_3^--N	5.0	0.8
ORG-N	0.02	-[a]
Effluent flow rate, m^3/day	34,900	4,040
pH	3.1	7.7
Reference	28	29

[a] Data not reported.

POTENTIAL ENVIRONMENTAL EFFECTS

Factors that bear on the evaluation of the potential environmental effects of a particular wastewater discharge include the hazard potential of the waste, discharge quantities, and type of receiving body. In this section, these parameters are quantified and then combined to determine another parameter called the source severity, which is used to measure the potential impact of a wastewater discharge on a receiving stream.

As mentioned previously, there are three types of nitrogen materials released in the effluent from nitrogen fertilizer plants: ammonia nitrogen, nitrate nitrogen, and organic nitrogen. Other minor contaminants, such as trace metals and water treatment compounds, are also present but more difficult to characterize because they are lower in concentration and dependent on individual plant design and operation.

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(28) Patterson, J. W., J. Brown, W. Duckert, J. Polson, and N. I. Shapira. State of the Art: Military Explosives and Propellants Production Industry. Volume II, Wastewater Characterization. EPA-600/2-76-213b, U.S. Environmental Protection Agency, Cincinnati, Ohio, August 1976. 273 pp.

(29) Fairall, J. M. Tennessee Valley Authority, Wilson Dam, Alabama--Nos. 1 and 2 Nitric Acid Units, Tennessee River. U.S. Department of the Interior, Tennessee Valley Authority and Federal Water Pollution Control Administration, Cincinnati, Ohio, May 1966. 12 pp.

Hazard Potential

Hazard potentials were arrived at by determining acceptable concentrations for each species in receiving streams. This concentration was then termed the hazard factor because higher concentrations may pose a potential hazard to aquatic life in the stream or to people who drink the water.

Established water quality criteria were used as hazard factors whenever possible, but in the absence of such criteria other data on health or toxic effects were used to determine estimated acceptable concentrations.

In general, the health effects data base is incomplete and the hazard factors include a safety factor to allow for more sensitive species. As more data become available, the hazard factors used in this report may be revised upward because the margin of safety is greater than necessary.

Ammonia Nitrogen--

When ammonia is present in water, a chemical equilibrium exists between un-ionized ammonia, ionized ammonia, and hydroxide ions as shown in Equation 15 (30).

$$NH_3^\circ + H_2O \rightleftarrows NH_3{\bullet}H_2O \rightleftarrows NH_4^+ + OH^- \quad (15)$$

At a given temperature, the percentage of un-ionized ammonia in solution can be found on Figure 14 (31).

Un-ionized ammonia (NH_3°) is the most toxic form of ammonia. A water quality criterion of 0.02 g/m^3, based on fish toxicity and including a ten-fold safety factor, has been assigned to un-ionized ammonia nitrogen (30). Thus 0.02 g/m^3 was chosen as the hazard factor for un-ionized ammonia nitrogen. At least one investigator has found the ionized form of ammonia (NH_4^+) to be toxic, but at levels much higher than those for NH_3. He estimates the toxicity of NH_4^+ to be less than 1/50 that of NH_3° (30). On this basis, a value of 1.00 g/m^3 was selected as a hazard factor for ionized ammonia nitrogen.

Nitrate Nitrogen--

The toxicity of nitrate nitrogen (NO_3^--N) in waters is due to its potential conversion to nitrite, which has been shown to be highly detrimental to the blood stream (30). A value of 10 g/m^3 has

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(30) Quality Criteria for Water. EPA-440/9-76-023, U.S. Environmental Protection Agency, Washington, D.C., July 1976. 501 pp.

(31) Thurston, R. V., et al. Aqueous Ammonia Equilibrium Calculations. Fisheries Bioassay Laboratory Technical Report No. 74, Montana State University, Bozeman, Montana, 1974. 18 pp.

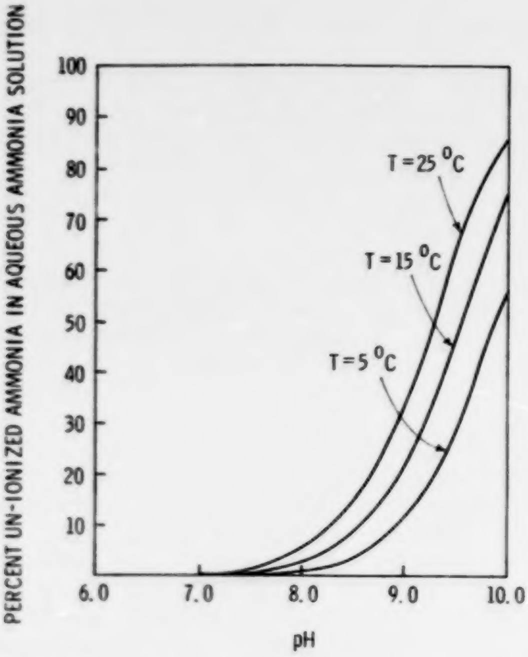

Figure 14. Percent un-ionized ammonia in aqueous ammonia solutions of zero salinity.

been established as a water quality criterion for nitrate nitrogen in domestic water supplies (30), and hazard factor of 10 g/m^3 was therefore used for nitrate nitrogen.

Organic Nitrogen

The predominant form of organic nitrogen (ORG-N) in the wastewater stream from a nitrogen fertilizer plant is urea. Other forms (e.g., amines or amides) of organic nitrogen may be present, as discussed previously, but will be considered negligible in light of the larger concentrations of urea.

An LD_{50} (lethal dose for a 50% kill of rabbits when dosed subcutaneously) of 3,000 mg/kg has been established for urea (32). The following equation has been derived to convert LD_{50} values for animals other than rats to hazard factors (33):

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(32) Registry of Toxic Effects of Chemical Substances, 1975 Edition. CDC-99-74-92, National Institute for Occupational Safety and Health, Rockville, Maryland, June 1975. 1296 pp.

(33) Reznik, R. B., E. C. Eimutis, J. L. Delaney, T. J. Hoogheem, S. R. Archer, J. C. Ochsner, W. R. McCurley, and T. W. Hughes. Source Assessment: Prioritization of Stationary Water Pollution Sources. EPA-600/2-77-107p, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1977. 137 pp.

$$\text{Hazard factor} = 2.25 \times 10^{-3} \times LD_{50} \qquad (16)$$

From this equation and the LD_{50} of 3,000 mg/kg, the hazard factor for urea in the effluent is calculated to be 6.75 g/m^3. This is equivalent to a measurement of 3.17 g/m^3 organic nitrogen (6.75 g/m^3 x 47 g N/100 g urea).

Discharge Quantities

Discharge quantities are determined by multiplying wastewater effluent flow rates and effluent concentrations. This gives a mass quantity for use in evaluation purposes, and does not consider the impact of in-plant dilution.

Receiving Body

Potential environmental effects are strongly dependent upon the type of receiving body into which plant effluent is discharged. Types of receiving bodies include sewers, dry ditches, canals, tributaries, large rivers, and lakes. In this report, the receiving body is defined to have a volumetric flow rate equal to the flow rate of the receiving body upstream of the plant plus the flow rate of the plant discharge. In many cases, the correction introduced by the flow rate of the plant discharge will prove negligible; however, it is an important consideration for discharge into a dry bed or small stream.

Probable receiving bodies for nitrogen fertilizer plants are listed in Appendix A, Table A-2. Sewers and lakes do not appear on the list and will not be considered further. Table A-3 lists the available data on pH and temperature for the receiving streams identified in Table A-2. Stream pH varied from 6.2 to 8.8 with an average of 7.6; temperatures ranged from 0°C to 33°C with an average of 16°C.

Source Severity

Source severity compares the concentration of a given pollutant in the receiving water as a result of discharge to the minimum concentration of the pollutant determined to be hazardous (hazard factor). In determining the source severity of a plant, the discharge quantity is compared to the receiving body flow rate times the hazard factor according to Equation 17.

$$S = \frac{V_D\ C_D}{\left(V_R + V_D\right)F} \qquad (17)$$

where S = source severity for a particular pollutant

V_D = wastewater effluent flow rate, m^3/s

C_D = concentration of particular pollutant, g/m^3

V_R = volumetric flow rate of receiving body above plant discharge, m^3/s

F = hazard factor for particular pollutant, g/m^3

Source severities were calculated for plants producing either ammonium nitrate or urea based on available data (Tables B-1 and B-2, Appendix B), and the results are presented in Tables 10 and 11. Nitrate nitrogen, organic nitrogen, and the two forms of ammonia, un-ionized ($NH_3°$-N) and ionized (NH_4^+-N), were the pollutant species considered in the source severity calculations. Receiving water pH and temperature are important parameters in determining the species of ammonia present. Therefore, severities were calculated at two receiving water pH levels, pH 7.6 and pH 9.0. These pH levels correspond to the average and maximum receiving water pH. The average receiving water temperature of 16°C was used in source severity calculations.

Source severities at each plant were calculated for each pollutant species based on the low and mean receiving body flow rates at the plant. The low flow rate represents a worst case example because it gives the smallest denominator in Equation 17, resulting in the largest source severity. The mean receiving body flow rate is indicative of average river flow conditions.

Source severities were also calculated for plants producing both urea and ammonium nitrate. In order to estimate these severities, Equation 17 was modified to Equation 18.

$$\frac{\left(V_{D_{AN}} C_{D_{AN}}\right) + \left(V_{D_U} C_{D_U}\right)}{F\left(V_{D_{AN}} + V_{D_U} + V_R\right)} = S \qquad (18)$$

where $V_{D_{AN}}$ = volumetric flow rate from ammonium nitrate plant, m^3/s

V_{D_U} = volumetric flow rate from urea plant, m^3/s

V_R = volumetric flow rate of receiving body, m^3/s

$C_{D_{AN}}$ = concentration of given pollutant in ammonium nitrate discharge, g/m^3

C_{D_U} = concentration of given pollutant in urea discharge, g/m^3

F = hazard factor for particular pollutant, g/m^3

S = source severity for particular pollutant

TABLE 10. CALCULATED SOURCE SEVERITIES FOR PLANTS PRODUCING AMMONIUM NITRATE (INCLUDING NITRIC ACID AND AMMONIA)

				Source severity									
				$NH_3°$-N				NH_4^+-N				NO_3^--N	
		Receiving body flow rate, m^3/s		Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate	Mean receiving body flow rate
Plant code	Production, metric tons/day	Low	Mean	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0		
S[a]	147	0.50	0.57	1.62	35.5	1.42	31.1	3.19	2.50	2.80	2.19	3.8×10^{-1}	3.3×10^{-1}
X	309	71	1,020	4.9×10^{-2}	10.3	3.4×10^{-3}	7.2×10^{-2}	9.5×10^{-2}	7.5×10^{-2}	6.6×10^{-3}	5.2×10^{-3}	7.6×10^{-3}	5.0×10^{-4}
Z	336	81	317	2.1×10^{-2}	4.7×10^{-1}	5.5×10^{-3}	1.2×10^{-1}	4.2×10^{-2}	3.3×10^{-2}	1.1×10^{-2}	8.6×10^{-3}	3.5×10^{-3}	9.0×10^{-4}
AA[b]	342	76.5	377	0	0	0	0	0	0	0	0	0	0
BB	241	303	3,210	4.4×10^{-3}	9.5×10^{-2}	4.2×10^{-4}	9.0×10^{-3}	8.6×10^{-3}	6.8×10^{-3}	8.2×10^{-4}	6.4×10^{-4}	8.2×10^{-3}	5.0×10^{-5}
FF	654	41	415	2.7×10^{-2}	6.0×10^{-1}	2.7×10^{-3}	5.9×10^{-2}	5.4×10^{-2}	4.2×10^{-2}	5.3×10^{-3}	4.2×10^{-3}	3.3×10^{-3}	3.2×10^{-4}
Average				2.5×10^{-2}	5.5×10^{-1}	3.0×10^{-3}	6.5×10^{-2}	5.0×10^{-2}	3.9×10^{-2}	5.9×10^{-3}	4.3×10^{-3}	5.6×10^{-3}	4.4×10^{-4}
Standard deviation				1.8×10^{-2}	3.8×10^{-1}	2.1×10^{-3}	4.6×10^{-2}	3.6×10^{-2}	2.8×10^{-2}	4.2×10^{-3}	3.3×10^{-3}	2.6×10^{-3}	3.6×10^{-4}

[a] Excluded from average to prevent low river flow rate (<1 m^3/s) from skewing the data.

[b] Excluded from average because plant is practicing zero discharge.

TABLE 11. CALCULATED SOURCE SEVERITIES FOR PLANTS PRODUCING UREA (INCLUDING AMMONIA)

Receiving water temperature equals 16°C

				Source severity									
				$NH_3°$-N				NH_4^+-N				ORG-N	
		Receiving body flow rate, m^3/s		Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate	Mean receiving body flow rate
Plant code	Production metric tons/day	Low	Mean	at ph 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0		
C	1,083	5,975	17,896	3.5×10^{-5}	7.6×10^{-4}	1.2×10^{-5}	2.5×10^{-4}	6.8×10^{-5}	5.4×10^{-5}	2.3×10^{-5}	1.8×10^{-5}	1.5×10^{-5}	4.9×10^{-6}
F	161	498	1,986	4.3×10^{-4}	9.5×10^{-3}	1.1×10^{-4}	2.4×10^{-3}	8.6×10^{-4}	6.7×10^{-4}	2.2×10^{-4}	1.7×10^{-4}	1.3×10^{-4}	4.5×10^{-5}
L	701	5,975	17,896	3.4×10^{-4}	7.5×10^{-3}	1.1×10^{-4}	2.5×10^{-3}	6.7×10^{-4}	5.3×10^{-4}	2.2×10^{-4}	1.8×10^{-4}	3.2×10^{-5}	1.1×10^{-5}
Average				2.7×10^{-4}	5.9×10^{-3}	7.7×10^{-5}	1.7×10^{-3}	5.3×10^{-4}	4.2×10^{-4}	1.5×10^{-4}	1.2×10^{-4}	5.9×10^{-5}	2.0×10^{-5}
Standard deviation				2.1×10^{-4}	4.6×10^{-3}	5.6×10^{-5}	1.3×10^{-3}	4.1×10^{-4}	3.2×10^{-4}	1.1×10^{-4}	9.0×10^{-5}	6.2×10^{-5}	2.2×10^{-5}

Input data for calculating source severities from composite plants are presented in Tables B-1 and B-2 and are summarized in Table 12. Source severity values for the composite plants for which adequate data are available are presented in Table 13.

Average source severity values are also presented in Tables 10, 11, and 13. Plants with low river flow rates (<1 m^3/s) are excluded from these averages in order not to skew the data and give an inaccurate view of the total industry. Because the river flow rate appears in the denominator of the source severity equation, low value can bias a set of data. Flow rate data listed in Table A-2 in Appendix A show that ∿10% of the plants in the industry discharge to rivers with mean flow rates of under 1 m^3/s.

Effluent data tabulated in Appendix B was supplied by industry to EPA as a basis for setting the effluent guideline standards as given in Table 14 (34). Standards for best practicable technology (BPT) are based on average effluent data from all plants within an industry category. Standards for best available technology (BAT) are based on those plants with the lowest effluent values. For the plants reporting data, 13 out of 31 ammonium nitrate plants and 12 out of 22 urea plants met the BPT standards. For BAT, 6 out of 31 ammonium nitrate plants and 10 out of 22 urea plants met the guidelines. It is expected that those plants that exceeded the guidelines have taken or are taking steps to reduce their effluent loading and come into compliance with the regulations.

Effluent guideline standards specify a certain effluent quality that must be achieved by plants within an industry. However, there are no restrictions in terms of the type of controls that must be used to meet the standards. Each plant may choose whatever control option is best suited to operating practices at its location, provided that final effluent quality is within the guidelines. In the case of ammonium nitrate manufacture, ion exchange technology is named as one example of BAT, but that is not intended to limit plants from using alternative control strategies if they wish.

Source severities can also be calculated for individual ammonia plants (34% of the nitrogen fertilizer plants) based on effluent data presented earlier in this section for pilot testing of a condensate steam stripper. Based upon the data presented in

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(34) Code of Federal Regulations, Title 40 - Protection of Environment, Chapter I - Environmental Protection Agency, Subchapter N - Effluent Guidelines and Standards, Part 418 - Fertilizer Manufacturing Point Source Category. Ammended regulations published in Federal Register 43(81):17821-17828, 1978.

TABLE 12. INPUT VALUES OF V_D, C_D, AND V_R USED TO CALCULATE SOURCE SEVERITY FOR COMPOSITE NITROGEN FERTILIZER PLANTS

Receiving water temperature equals 16°C

Plant code	Urea			Ammonium nitrate			Receiving body flow rate, m^3/s	
	V_D, m^3/s	$C_D(NH_3\text{-}N)$, g/m^3	$C_D(ORG\text{-}N)$, g/m^3	V_D, m^3/s	$C_D(NH_3\text{-}N)$, g/m^3	$C_D(NO_3^-\text{-}N)$, g/m^3	$V_R(Lo)$	$V_R(Mean)$
B	0.000441	68	-[a]	0.00195	65	72	377	1,305
G	0.1108	18	1	0.1211	17.8	3.7	5	90
H	0.0016	1,030	82	0.0009	9,111	951	0.05	0.68
I	0.0736	5	11	0.00286	141	92.9	0.5	4
J	0.0045	83	104	0.0263	83.1	71.6	205	448
M	0.0074	241	455	0.00113	2,110	2,900	50	177
N	0.002	198	3,640	0.0007	0.1	0.1	518	1,420
P	0.0193	308	-[a]	0.0205	229	229	227	1,005
R	0.2174	92	17	0.252	17.5	19.0	317	1,190
S	0.0515	291	16	0.0840	291	75.3	5,975	17,896
T	0.0193	222	160	0.0034	5,200	780	498	1,986
U	0.00907	112	112	0.0507	149	89	156	331
V	0.0213	495	1,169	0.0591	495	148	6,400	19,930

[a] Not available.

TABLE 13. CALCULATED SOURCE SEVERITIES FOR PLANTS PRODUCING AMMONIUM NITRATE AND UREA (INCLUDING NITRIC ACID AND AMMONIA)

	Source severity											
	$NH_3°$-N				NH_4^+-N				NO_3^--N		ORG-N	
	Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate		Mean receiving body flow rate		Low receiving body flow rate	Mean receiving body flow rate	Low receiving body flow rate	Mean receiving body flow rate
Plant code	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0	at pH 7.6	at pH 9.0				
B	2.1×10^{-4}	4.6×10^{-3}	6.0×10^{-5}	1.3×10^{-3}	4.1×10^{-4}	3.2×10^{-4}	1.2×10^{-4}	9.4×10^{-5}	1.2×10^{-4}	3.4×10^{-5}	–[a]	–[a]
G	4.0×10^{-1}	8.74	2.3×10^{-2}	5.1×10^{-1}	7.9×10^{-1}	6.2×10^{-1}	4.6×10^{-2}	3.6×10^{-2}	8.6×10^{-3}	5.0×10^{-4}	6.7×10^{-3}	4.0×10^{-4}
H[b]	98.5	2,167	7.24	159 184		145	13.5	10.7	1.71	1.3×10^{-1}	8.3×10^{-1}	6.1×10^{-2}
I[b]	6.7×10^{-1}	14.8	9.4×10^{-2}	2.00 1.33		1.05	1.9×10^{-1}	1.5×10^{-1}	5.3×10^{-2}	6.6×10^{-3}	5.2×10^{-1}	6.5×10^{-2}
J	6.2×10^{-3}	1.4×10^{-1}	2.9×10^{-3}	6.3×10^{-2}	1.2×10^{-2}	9.7×10^{-3}	5.7×10^{-3}	4.4×10^{-3}	9.2×10^{-4}	4.2×10^{-4}	7.0×10^{-4}	3.0×10^{-4}
M	4.2×10^{-2}	9.2×10^{-1}	1.2×10^{-2}	2.6×10^{-1}	8.2×10^{-2}	6.5×10^{-2}	2.3×10^{-2}	1.8×10^{-2}	6.6×10^{-3}	1.8×10^{-3}	2.1×10^{-2}	6.0×10^{-3}
N	3.8×10^{-5}	8.4×10^{-4}	1.4×10^{-5}	3.1×10^{-4}	7.6×10^{-5}	6.0×10^{-5}	2.8×10^{-5}	2.2×10^{-5}	$<10^{-6}$	$<10^{-6}$	4.4×10^{-4}	1.6×10^{-4}
P	2.3×10^{-2}	5.1×10^{-1}	5.3×10^{-3}	1.2×10^{-1}	4.6×10^{-2}	3.6×10^{-2}	1.1×10^{-2}	8.2×10^{-3}	2.0×10^{-4}	4.9×10^{-5}	–[b]	–[b]
R	3.8×10^{-2}	8.4×10^{-1}	1.0×10^{-2}	2.2×10^{-1}	7.6×10^{-2}	6.0×10^{-2}	2.0×10^{-2}	1.6×10^{-2}	1.5×10^{-3}	4.0×10^{-4}	3.7×10^{-3}	9.8×10^{-4}
S	3.3×10^{-3}	7.2×10^{-2}	1.1×10^{-3}	2.4×10^{-2}	6.5×10^{-3}	5.1×10^{-3}	2.2×10^{-3}	1.7×10^{-3}	1.1×10^{-4}	3.5×10^{-5}	4.4×10^{-5}	1.4×10^{-5}
T	2.2×10^{-2}	4.8×10^{-1}	5.5×10^{-3}	1.2×10^{-1}	4.4×10^{-2}	3.5×10^{-2}	1.1×10^{-2}	8.6×10^{-3}	5.3×10^{-4}	1.3×10^{-4}	2.0×10^{-3}	4.9×10^{-4}
U	2.7×10^{-2}	6.0×10^{-1}	1.3×10^{-2}	2.8×10^{-1}	5.4×10^{-2}	4.3×10^{-2}	2.6×10^{-2}	2.0×10^{-2}	2.9×10^{-3}	1.4×10^{-3}	2.0×10^{-3}	9.7×10^{-4}
V	3.1×10^{-3}	6.8×10^{-2}	1.1×10^{-3}	2.2×10^{-2}	6.2×10^{-3}	4.8×10^{-3}	2.0×10^{-3}	1.6×10^{-3}	1.1×10^{-4}	4.4×10^{-5}	1.2×10^{-3}	4.0×10^{-4}
Average	5.1×10^{-2}	1.12	6.7×10^{-3}	1.5×10^{-1}	1.0×10^{-1}	8.0×10^{-2}	1.3×10^{-2}	1.0×10^{-2}	2.0×10^{-3}	4.4×10^{-4}	4.2×10^{-3}	1.1×10^{-3}
Sd	1.2×10^{-1}	2.55	7.2×10^{-3}	1.6×10^{-1}	2.3×10^{-1}	1.8×10^{-1}	1.4×10^{-2}	1.1×10^{-2}	3.0×10^{-3}	6.1×10^{-4}	6.6×10^{-3}	1.9×10^{-3}

Note.—Sd = standard deviation.

[a] Not available.

[b] Excluded from average to prevent low river flow rate (<1 m^3/s) from skewing the data.

TABLE 14. EFFLUENT GUIDELINES (34)

Product	Effluent species	Effluent guideline, g/kg: Best practicable technology: Daily maximum	Effluent guideline, g/kg: Best practicable technology: Monthly average	Effluent guideline, g/kg: Best available technology: Daily maximum	Effluent guideline, g/kg: Best available technology: Monthly average
Urea (solutions)	NH_3-N	0.95	0.48	0.53	0.27
	ORG-N	0.61	0.33	0.45	0.24
Urea (prilled or granulated)	NH_3-N	1.18	0.59	0.53	0.27
	ORG-N	1.48	0.80	0.86	0.46
Ammonium nitrate	NH_3-N	0.73	0.39	0.08	0.04
	NO_3-N	0.67	0.37	0.12	0.07

Table 4 and low and mean receiving body flow rates of 6 6 m^3/s and 18 m^3/s, respectively, source severities for ammonia NH_3°) and ammonium (NH_4^+) were calculated and are presented in Table 15. Plants with less efficient steam strippers could have source severities higher by up to a factor of ten under the same conditions (i.e., same size plant and same receiving stream).

TABLE 15. CALCULATED SOURCE SEVERITIES FOR A CONDENSATE STEAM STRIPPER OF AN AMMONIA PLANT

Receiving water temperature equals 16°C

	Source severity: NH_3°-N	Source severity: NH_4^+-N
Low receiving water flow rate:		
Receiving water pH = 7.6	1.13×10^{-2}	2.61×10^{-2}
Receiving water pH = 9	2.76×10^{-1}	2.08×10^{-2}
Mean receiving water flow rate:		
Receiving water pH = 7.6	3.77×10^{-3}	8.71×10^{-3}
Receiving water pH = 9	9.21×10^{-2}	6.94×10^{-3}

For those plants that recycle process condensate rather than discharge it, the source severities should still be similar, because the condensate must be purified before use as boiler feedwater. In this case spent regenerant from the ion exchange units used for purification becomes the discharge stream. However, material balance considerations show that the discharge stream must contain the same amount of NH_3-N as the condensate from the steam stripper.

Other Considerations

In applying the source severity equation (Equation 18), it is assumed that the greatest impact occurs where the discharge is mixed with the receiving stream. In reality, the situation may be different when considering NH_3-N and urea. Urea and ammonia put an oxygen demand on the stream some distance downstream as NH_3 and urea are naturally oxidized by nitrifying bacteria to NO_2^-, NO_3^-, and CO_2. If the receiving stream is low in dissolved oxygen and has a low capacity to reoxygenate, toxicity to aquatic life in the stream may be caused by an oxygen depletion some distance downstream from the discharge rather than by ammonia or urea toxicity near the discharge point.

To determine the potential effect due to oxygen depletion by urea and ammonia, the following assumptions are made:

- No reaeration of the receiving body takes place while NH_3 and urea are being oxidized.
- All of the entering NH_3 and urea is completely oxidized to CO_2 and NO_3^- by the oxygen in the receiving body.
- 2 moles of oxygen are required to oxidize 1 mole of NH_3, or 3.76 g of O_2 per gram of NH_3.
- 7 moles of oxygen are required to oxidize 1 mole of urea, or 8 g of O_2 per gram of ORG-N.

In addition, the following average flow characteristics describing the wastewater from a composite ammonium nitrate urea plant, as shown in Tables B-5 and B-6, are used to determine the worst case flow conditions:

- Flow rate of the discharge stream originating from the urea plant is 0.0399 m^3/s; it contains 120 g/m^3 NH_3-N and 90 g/m^3 ORG-N.
- Flow rate of the discharge stream originating from the ammonium nitrate plant is 0.0327 m^3/s; it contains 482 g/m^3 NH_3-N.
- Flow rate of the receiving stream is 771 m^3/s.

With the above conditions, the oxygen demand can be calculated as follows:

$$\text{oxygen demand} = \frac{\Sigma(\text{pollutant discharge rate})(\text{molar ratio})}{\text{receiving body flow rate}}$$

$$\frac{\{[(482)(0.0327)] + [(120)(0.0399)]\}3.76 + \{[(90)(0.0399)]\}8}{771 + .0327}$$

$$= 0.14\ \text{g/m}^3\ O_2$$

Considering that this approximates a worst case situation, the oxygen concentration demand is not significant when compared to normal oxygen concentrations (∿10 g/m^3), and toxicities are considered more important parameters in evaluating the impact of effluent discharge on stream quality.

Wastewater constituents other than nitrogen derivatives were reported by some plants, and they are listed in Table 16. As can be seen, there are no other significant constituents discharged by ammonium nitrate plants, urea plants, or nitrogen fertilizer complexes. Source severities were therefore not calculated for these minor constituents.

TABLE 16. MINOR CONSTITUENTS PRESENT IN PLANT EFFLUENTS

	Ammonium nitrate plants					Urea plants		Plants producing both urea and ammonium nitrate						
Parameter	R	X	Z	JJ	II	A	R	B	E	G	K	N	P	Q
pH	7.2	7.7	6.3	7.6	6.3	7.1	7.5	8.2	7.2	8.4	7.4	8.3	7.6	8.0
Temperature, °C	13					13								
Total suspended solids, g/m^3			29	11	1.5			34		32	4	10	7	-
Total dissolved solids, g/m^3				18										
Chemical oxygen demand, g/m^3			67		29		100			74		12		
5-Day biochemical oxygen demand, g/m^3		8		<3	-									-
Total hardness as $CaCO_3$, g/m^3	8					16								
Calcium hardness as $CaCO_3$, g/m^3	-					0								
Magnesium hardness as $CaCO_3$, g/m^3	10					16								
Total alkalinity as $CaCO_3$, g/m^3	-					-								
Sulfate (SO_4), g/m^3	2					0								
Chloride (Cl), g/m^3	4					3								
Sodium (Na), g/m^3	3					5								
Total iron (Fe), g/m^3	-					0.03								
Total phosphate (PO_4), g/m^3	0.7					0.7								
Manganese (Mn), g/m^3	0.1					0								
Copper (Cu), g/m^3	0.12					0.12		0.3						
Chromate (Cr), g/m^3	0					-						0.52		-
Silica (SiO_2), g/m^3	-					-								
Oil and grease, g/m^3												1.1		
Nickel (Ni), g/m_3	-					-								
Zinc (Zn), g/m^3	0					0.02								-
Cyanide (Cn^-), g/m^3		0.12												
Residual Cl_2, g/m^3		3.6									0.7			

Note.—Blanks indicate data not available, and dashes indicate reported plant intake concentration greater than reported effluent concentration.

SECTION 5

CONTROL TECHNOLOGY

Control technology as applied to the wastewater effluent from nitrogen fertilizer plants is used basically to control the following primary contaminants: ammonia nitrogen, organic nitrogen and nitrate nitrogen. Control technologies may focus on a particular process discharge or may be applicable to an entire plant complex.

TYPES OF CONTROL

Containment

Containment is used basically to control effluents from nonpoint sources such as pump seal leaks, spills, and plant washdowns. It is achieved by using a small dike or by proper drainage design. If the area is not drained but simply enclosed by a dike (usually less than 0.15 m high), evaporation controls the effluent level and no discharge occurs. If the area is drained, however, additional control technology is needed just as if the effluent were from a point source.

Containment is used to some degree at almost every nitrogen fertilizer plant. The degree of application may range from a simple dike around a couple of pumps to entire areas drained by an underground system. Newer plants are anticipated to have an increasing amount of containment as an awareness of the level of nonpoint source effluents increases. In addition, older plants often incorporate a containment system in newly installed control systems.

In any situation where wastewaters are contained in ponds or behind dikes, there is the possibility that materials can leach or percolate through the soil into underground water supplies. Nothing is presently known about whether this may be a potential problem at nitrogen fertilizer plants.

Steam Stripping

Steam stripping is used on process condensate from nitrogen fertilizer plants for the removal of ammonia, carbon dioxide and methanol. The condensate stripper in its simplest form passes low pressure steam countercurrent to the condensate in a packed or tray tower. Overhead product from the stripper is vented directly to the atmosphere or recovered for the value of its ammonia content. Stripping occurs at a pressure adapted to the pressure of the recirculation section if offgases are to be recovered. The content of ammonia in the stripped condensate ranges from 5 g/m^3 to 100 g/m^3 and is highly dependent on the amount of steam and the pH of the contaminated feed condensate (25). In neutral solutions ammonia exists mainly as the ammonium ion while at higher pH (11 to 12) ammonia exists as dissolved gas. Residual methanol in stripped condensate varies but usually is in the range of 20 g/m^3 to 100 g/m^3 (9). Stripped condensate is either discharged into a receiving stream or used as cooling water makeup or as boiler feedwater.

The ammonia concentration of the effluent is lowered by increasing the amount of stripping steam. However, increasing steam usage will dilute the overhead product and may adversely affect the water balance of the recirculation system. Addition of a refluxing system can be used in producing a concentrated overhead product from dilute (approximately 1,000 g/m^3) condensate streams. The more concentrated overhead may then be recycled. Either one of these modifications may be uneconomical or produce a stream incompatible with present operation.

Under a grant awarded through the U.S. Environmental Protection Agency (EPA), the Louisiana Chemical Association (LCA) participated in the study and development of a reflux system (35). A schematic diagram of the pilot steam stripper used is shown in Figure 15 (35). The stripper was operated as a fractionator, as overhead would be totally condensed and reflux provided. The pilot stripper achieved 98% and 99.8% removal of ammonia and methanol, respectively. Maximum overhead ammonia concentration was 6% (60,000 g/m^3) with a minimum bottoms concentration of 20 g/m^3 (35). Process condensate with an average concentration in the range of 1,000 g/m^3 ammonia and 600 g/m^3 methanol was used in the process. In this study the overhead condensate was sent to the primary reformer and incinerated. The overhead may also be recycled as feedstock, but this alternative requires more energy.

Air Stripping

Air stripping of ammonia from wastewater has in the past been focused primarily in the municipal wastewater treatment area. Its potential application to nitrogen fertilizer plant effluent is direct because in both cases the objective is to remove

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(35) Romero, C. U., and F. H. Yocum. Treatment of Ammonia Plant Process Condensate. In: Proceedings of the Fertilizer Institute Environmental Symposium (New Orleans, Louisiana, January 13-16, 1976), The Fertilizer Institute, Washington, D.C. pp. 45-89.

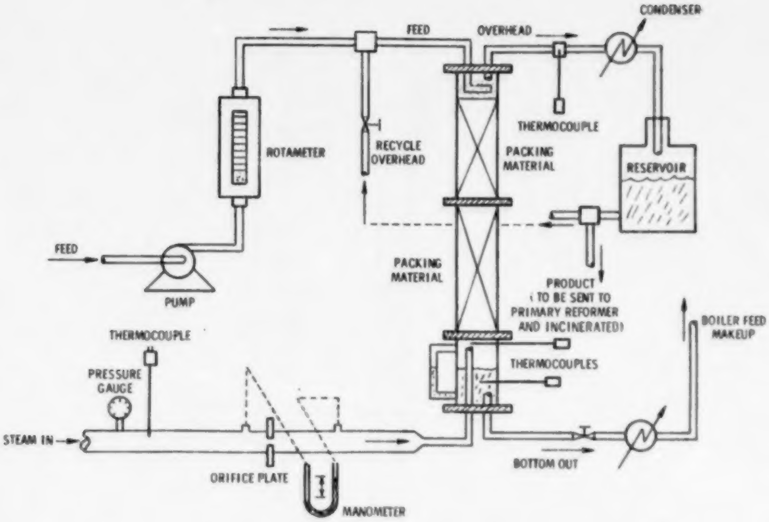
CONDENSER
FEED
OVERHEAD
THERMOCOUPLE
ROTAMETER
RECYCLE OVERHEAD
PACKING MATERIAL
RESERVOIR
FEED
PUMP
PACKING MATERIAL
PRODUCT (TO BE SENT TO PRIMARY REFORMER AND INCINERATED)
BOILER FEED MAKEUP
THERMOCOUPLE
PRESSURE GAUGE
THERMOCOUPLES
STEAM IN
BOTTOM OUT
ORIFICE PLATE
MANOMETER

Figure 15. Model of pilot steam stripper (35).

ammonia. Currently at least one ammonia plant practices air stripping to remove ammonia from process condensate (36).

Some testing has been done on air stripping ammonium nitrate effluent. These tests have shown that the ammonia concentrations in the stripping air did not exceed 10 mg/m³ (25). Information on the percent removal of ammonia in the effluent stream as a function of operating parameters is not available. Some of the critical parameters are bed depth, transfer medium, surface loading rate, and proper pH. Disadvantages to air stripping are the decrease in efficiency due to cold weather operation and the deposition of calcium carbonate scale from the water on the column packing or internals resulting in plugging (25). Figure 16 is a schematic of a tower used for ammonia air stripping.

Urea Hydrolysis

This treatment system is designed to process condensate containing urea by converting the urea through a series of intermediate products back to ammonia and carbon dioxide. The ammonia and CO_2 are then driven off with steam.

Decomposition of urea into its basic components may be effected in two methods: biological conversion or thermal hydrolysis. In the biological process, urease enzyme produced by *Bacillus Pasteuri* acts to decompose the urea into NH_3 and CO_2 (37). This

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(36) Personal communication with T. W. Segar, N-ReN Corporation, Cincinnati, Ohio, June 1978.

(37) Smit, A. C. M., and P. U. C. Kaasenbrood. Treatment of Urea-Plant Effluents. Industrial Wastes, 22(5):44-47, 1976.

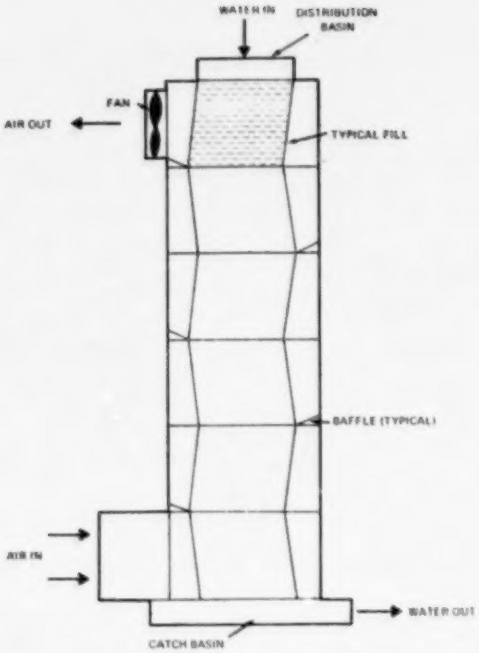

Figure 16. Ammonia/condensate air stripping (25).

decomposition takes place on a fixed carbon bed that serves as a support for the aerobic bacteria. Oxygen and nutrients needed by the bacteria are added, because they are not supplied in the process condensate feed. Major drawbacks of this biological treatment system are the following:

- Air supplied to support bacterial growth must be washed free of ammonia.
- The biological process is very sensitive to fluctuations in the feed streams.
- Much time is needed to achieve optimum column performance.

As a result of these major drawbacks, no biological conversion systems are currently in operation.

In the thermal hydrolysis process, a single tower is used for both hydrolysis and desorption. Heated urea process condensate is fed directly to the stripper tower where dissolved urea is hydrolyzed to ammonium carbamate, and ammonium carbamate is decomposed to gaseous ammonia and CO_2, which exit overhead. This process is carried out at temperatures above 100°C and under pressures of up to 1.8 MPa (25). Overhead vapors containing the ammonia and CO_2 have a relatively low concentration of water vapor and can be returned to the urea plant for recovery without affecting the reactor water balance or increasing steam consumption in the ammonium carbamate recycle loop.

A somewhat modified hydrolysis stripping unit has been developed by CF Industries and is shown diagramatically in Figure 17 (38). In this operation, the condensate enters a low pressure boiler operating at 57 kPa and 85°C. The condensate is evaporated and the urea in the stream is hydrolyzed to ammonia and CO_2. Approximately 93% of the vapor goes through the condenser to the top of the stripping column. The remainder is discharged to the lower section. Approximately 7% of the condensate water containing about 86% of the ammonia and carbon dioxide are recycled to the process through a condenser (38).

The bottom stream containing the remainder of the water, ammonia, and CO_2 goes to a deaerator operating at 448 kPa and 148°C for removal of approximately 85% of the residual contaminants. The bottom stream from this unit is of sufficient quality to go to a high pressure boiler (38).

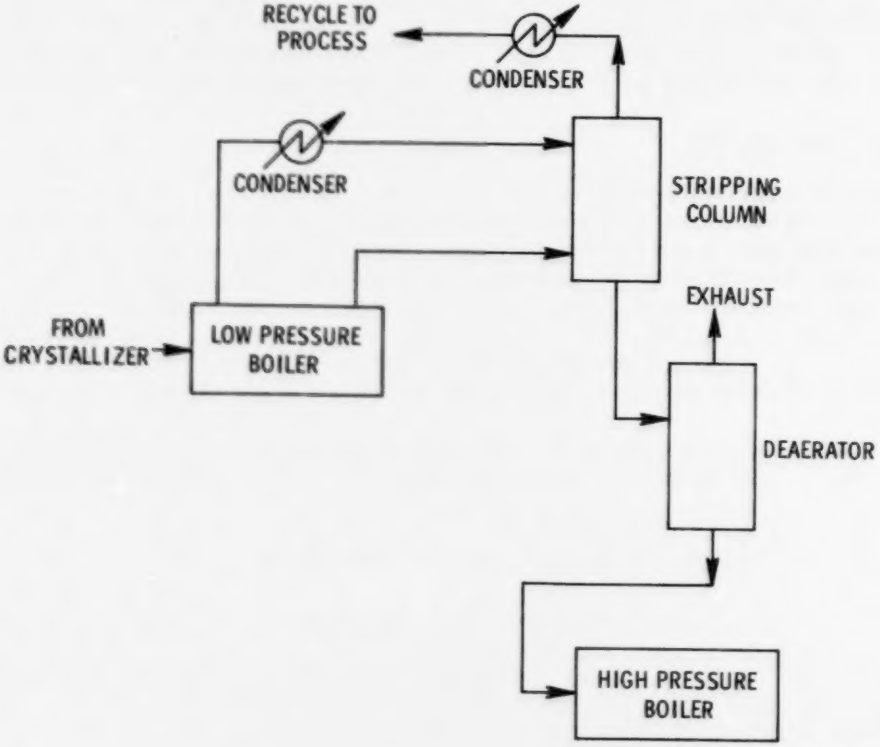
RECYCLE TO PROCESS
CONDENSER
CONDENSER
STRIPPING COLUMN
EXHAUST
FROM CRYSTALLIZER
LOW PRESSURE BOILER
DEAERATOR
HIGH PRESSURE BOILER

Figure 17. Method for Treatment of Urea Crystallizer Condensate (38).

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(38) Van Moosel, W. H. Method for Treatment of Urea Crystallizer Condensate. U.S. Patent 3,922,222 (to CF Industries, Inc.), November 25, 1975.

A number of hydrolysis stripper units are now in operation and more are expected as urea producers strive to meet plant effluent standards for 1977 and 1983. Three Technip SD Plants hydrolyzer strippers already are operating in the United States. The newest is at Atlas Powder's 272-metric ton/day plant in Joplin, Missouri, which started up earlier in 1977. It uses a 14-m high tower that is 1.14 m in diameter to handle waste flows with ammonia levels up to 15% and urea up to 3% by weight. An ammonia stripper at the 236-metric ton/day Cooperative Farm Chemicals Assn. urea plant in Lawrence, Kansas went on stream in 1972 (39). These two units are retrofits to existing plants. Technip SD Plants' units will reduce effluent urea and ammonia to 20 g/m^3 (39). Vistron's only operating unit is at its own 635-metric ton/day urea plant in Lima, Ohio, but the Vistron system will be used in the 907-metric ton/day urea plant being built in Kenai, Alaska, as a joint venture of Union Oil's Collier Carbon & Chemicals Corp. subsidiary and Mitsubishi Gas Chemical (39). Vistron's hydrolysis unit can handle 15% or more ammonia and up to 3% by weight of urea and bring effluent levels down to 60 g/m^3 of urea and 30 g/m^3 of NH_3 (39). CF Industries has two of their own systems installed as retrofits to existing plants. Agrico has one unit in service.

Biological Treatment

A possible treatment mechanism for the removal of ammonia and ammonium nitrate from process condensate involves biological nitrification and denitrification. This process, applied for years in the treatment of municipal wastes, is based on the reaction of ammonia nitrogen with oxygen in an aerated pond or basin to form nitrates via biological oxidation. The nitrates are in turn reacted in an anaerobic environment in the presence of a biodegradable carbon compound to form elemental nitrogen.

In the nitrification process, ammonia is oxidized aerobically to nitrite (NO_2^-) and then to nitrate (NO_3^-). The following equations apply:

$$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O \qquad (19)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (20)$$

In addition to requiring an adequate supply of oxygen and warm temperatures, the rate of nitrification is strongly pH dependent. The maximum nitrification rate is attained at a pH of 8.0. This falls to 90% of maximum at pH's of 7.8 and 9.0, and only 50% at a pH of 7.0 (40). Because the production of acidity is part of the biological metabolism, alkalinity must be supplied to maintain an operable system.

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(39) Urea Makers Can Strip Away Waste Problems. Chemical Week, 120(14):33-34, 1976.

In the denitrification process, nitrate is anaerobically converted to nitrogen gas. Anaerobic micro-organisms cause the nitrates and available carbon to be broken down into nitrogen gas and CO_2. Methanol has been the most successful carbon source used, but work has also been done using sugar, acetic acid, methane, sewage sludge, and raw wastewater as the source. Using methanol the pertinent equation is:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2\uparrow + 5CO_2\uparrow + 7H_2O + 6OH^- \qquad (21)$$

Because effluents from nitrogen fertilizer plants do not normally contain a carbon source for the microorganisms, additional carbon would have to be supplied. This could introduce another environmental problem not originally present.

Ion Exchange

Figure 18 is a schematic diagram of the Chemical Separations Corporation continuous ion exchange process. In this process, ammonium nitrate bearing fertilizer wastes flow to a strongly acidic cation exchange unit where the ammonium ion combines with the resin while the H^+ ion combines with the nitrate ion to form nitric acid. The wastewater then flows to an anion unit where the nitrate ion combines with the resin and water is formed. The following equations apply (25):

$$\text{Cation:}\quad NH_4NO_3 + R_2H \rightarrow R_2NH_4 + HNO_3 \qquad (22)$$

$$\text{Anion:}\quad HNO_3 + R_2OH \rightarrow R_2NO_3 + H_2O \qquad (23)$$

The resulting water stream can be discharged to a receiving body or used as boiler feed water or cooling tower makeup. A representative feed and treated water effluent analysis is shown in Table 17 (41).

The CHEM-SEPS® ion exchange system is operated in a continuous manner. Ion exchange resins, pulsed hydraulically through a closed loop, are divided into three sections for simultaneous demineralization of wastewater, washing of resin, and regeneration. To regenerate the cation and anion resin beds, 22% nitric

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(40) Mioduszewski, D. Ammonia Removal - What's Best? Water & Wastes Engineering, 12(7):34-46, 1975.

(41) Bingham, E. C., and R. C. Chopra. A Closed Cycle Water System for Ammonium Nitrate Products. Brochure, Chemical Separations Corporation, Oak Ridge, Tennessee, 1971. 11 pp.

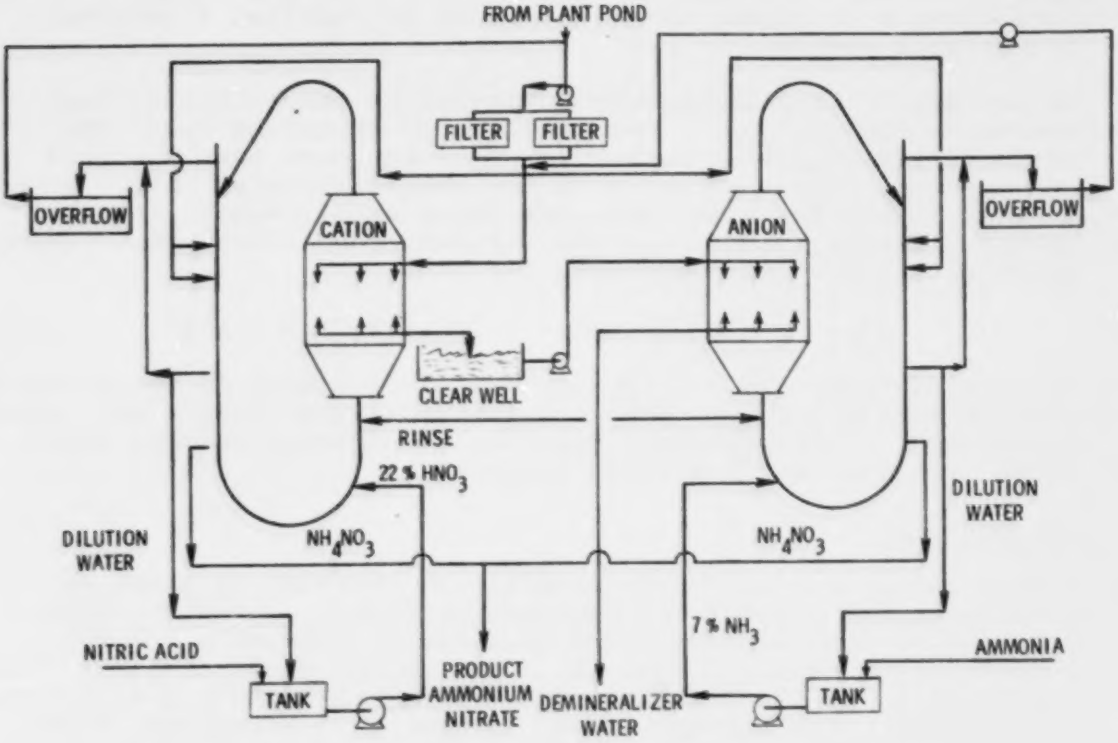
FROM PLANT POND
FILTER
FILTER
OVERFLOW
CATION
ANION
OVERFLOW
CLEAR WELL
RINSE
22 % HNO_3
NH_4NO_3
NH_4NO_3
DILUTION WATER
DILUTION WATER
7 % NH_3
NITRIC ACID
TANK
PRODUCT AMMONIUM NITRATE
DEMINERALIZER WATER
TANK
AMMONIA

Figure 18. Continuous ion exchange process (25).

TABLE 17. REPRESENTATIVE WASTE AND TREATED WATER ANALYSIS FROM ION EXCHANGE (41)

Component	Influent, g/m^3	Effluent, g/m^3
Ammonia (NH_3)	340	2 to 3
Magnesium (Mg^{++})	4.8	-
Calcium (Ca^{++})	60	-
Sodium (Na^+)	0	-
Nitrate (NO_3^-)	1,240	7 to 11
Chloride (Cl^-)	53	-
Sulfate (SO_4^-)	72	-
pH	5 to 9	5.9 to 6.4
Silica (SiO_2)	15	15

Ammonium nitrate removal is 99.4%.

acid (HNO_3) and 7% NH_3 solutions are used, respectively. The resulting streams will contain an amminium nitrate concentration of 10% to 20%. The application of the Chem-Seps process is limited to those manufacturers who have an outlet for this recovered ammonium nitrate solution. Many manufacturers feel that there are certain materials in the receovered solution that would prohibit evaporating this recovered solution to dryness because of their sensitizing qualities (i.e., they render the solid product more susceptible to explosions). This is of particular concern to those manufacturers who use some or all of their ammonium nitrate in the manufacture of explosives.

Ion exchange appears to be the growing technique by which ammonium nitrate plant effluents are being treated and is named as the best available technology for these plants in the amended effluent date guidelines of 1978 (34). As of January 1976, 10 major ammonium nitrate plants had decided to utilize the Chem-Seps process (Table 18) (42).

TABLE 18. PLANT LOCATIONS USING ION EXCHANGE (42)

Plant	Location
Hercules, Inc.	Louisiana, MO
Mississippi Chemical Co.	Yazoo City, MS
American Cyanamid Co.	Hannibal, MO
Indiana Army Ammunition Plant (ICI America)	Charleston, IN
Standard Oil Co. of Ohio Vistron Division	Lima, OH
W. R. Grace & Co.	Wilmington, NC
Joliet Army Ammunition Plant	Joliet, IL
Illinois Nitrogen Corp.	Marseilles, IL
CF Industries, Inc.	Chattanooga, TN
CF Industries, Inc.	Tunis, NC

Condensate Reuse

A potential control technology involves the direct recycle of neutralizer condensate as a feed stream. The effluent stream from the condensed neutralizer exhaust at an ammonium nitrate plant, for example, could potentially be used as a feed to the absorption column in the adjacent nitric acid plant. The value of the nitrate content in the wastewater would then be realized. Figure 19 is an example of ammonium nitrate effluent utilization.

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(42) Brennan, J. F. The Chem-Seps Nitrogen Recovery Process: A Pollution Solution that Works. In: Proceedings of The Fertilizer Institute Environmental Symposium (New Orleans, Louisiana, January 13-16, 1976), The Fertilizer Institute, Washington, D.C. pp. 217-249.

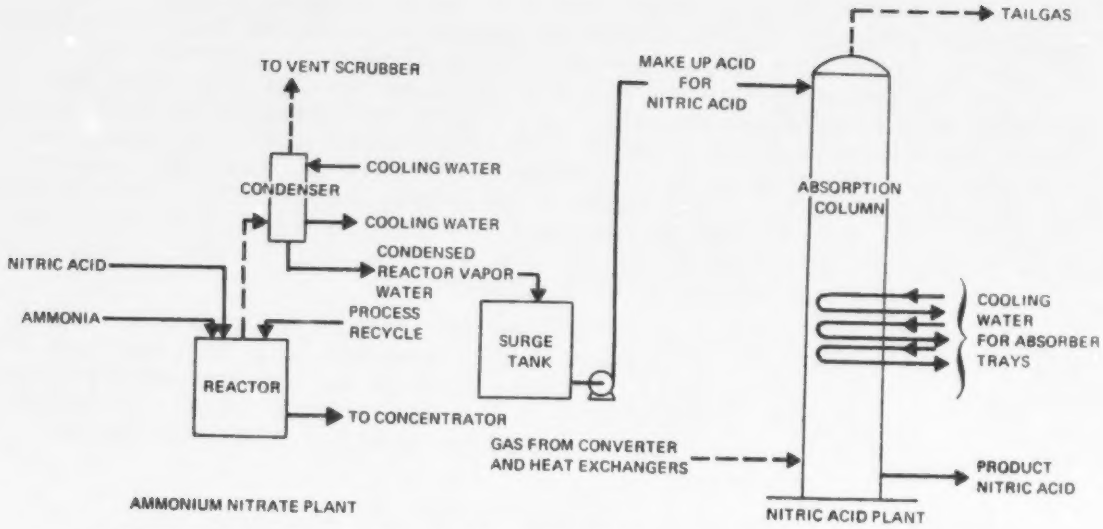
TAILGAS
TO VENT SCRUBBER
MAKE UP ACID FOR NITRIC ACID
COOLING WATER
CONDENSER
ABSORPTION COLUMN
COOLING WATER
CONDENSED REACTOR VAPOR WATER
NITRIC ACID
AMMONIA
PROCESS RECYCLE
SURGE TANK
COOLING WATER FOR ABSORBER TRAYS
REACTOR
TO CONCENTRATOR
GAS FROM CONVERTER AND HEAT EXCHANGERS
PRODUCT NITRIC ACID
AMMONIUM NITRATE PLANT
NITRIC ACID PLANT

Figure 19. Ammonium nitrate effluent utilization (9).

DEGREE OF APPLICATION

Production of nitrogen fertilizers often occurs in a complex of several manufacturing lines. The effluent is therefore composed of the individual effluents originating with each component process. As a result it is difficult to compose an exact listing of control techniques applied on a plant-by-plant basis.

Table 19 provides estimates of the degree of utilization of various nitrogen control technologies by industry segments. Air stripping of ammonia, condensate reuse and biological treatment of effluents are not included in Table 19 as they are now rarely applied to effluent control.

TABLE 19. DEGREE OF UTILIZATION OF NITROGEN CONTROL TECHNOLOGIES BY INDUSTRY SEGMENT

Product	Steam stripping	Ion exchange	Hydrolysis	Containment
Ammonium nitrate	M	L	NA	M
Urea	M[a]	NA	M	M
Ammonia	H	NA	NA	M

L - low utilization
M - medium utilization
H - high utilization
NA - not applicable

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[a] Steam stripping is often used in conjunction with urea hydrolysis at a urea plant.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

The technology utilized in the production of various major nitrogen-based fertilizers or components; i.e., ammonia, ammonium nitrate, urea, and nitric acid, is well established. For example,there have been no major breakthroughs in the production of ammonium nitrate since high density prilling was begun in the early 1960's. Nitric acid and urea production have followed a similar pattern of no major change in production technology.

Ammonia production further illustrates the static aspects of technology development when one considers that in the United States, 98% of the synthetic ammonia is produced by steam reforming natural gas. Six plants representing less than 2% of domestic production use hydrogen feedstock obtained from salt water electrolysis plants. Foreign processes for ammonia production include: use of naphtha and other light hydrocarbons for feedstock, partial oxidation of heavier hydrocarbons (petroleum oil or distillates), cryogenic recovery of hydrogen from petroleum refinery gases, and gasification of coal or coke. These production techniques are not used in the United States because of their high capital and operating costs compared to the low prices and availability of natural gas in this country.

EMERGING TECHNOLOGY

Ammonia Manufacturing

As long as natural gas is available and cheaper than oil, plants in the United States will continue to use the catalytic steam reforming process. However, because of the uncertainty in natural gas supply and prices, several companies are considering other production techniques.

Because of natural gas curtailments, about 50% of the plants are beginning to fire No. 2 fuel oil in the radiant heat section of the primary reformer during winter months (43-45). If gas supplies continue to dwindle, this practice probably will be extended to full annual operation.

In terms of feedstock substitution, estimates indicate that conversion from natural gas to naphtha would cost 50% to 100% of the original expense of a new plant (46, 47). For example, a new 900-metric ton/day ammonia plant built to use naphtha would cost 15% more than one built to operate on natural gas because additional desulfurization and carbon removal equipment would have to be installed to treat the dirtier feedstock (46).

Ammonium Nitrate

Changes in neutralizer operation and construction are among the most significant developments which may affect effluent quality. Different designs have been proposed for the control of air emissions (1).

Urea

Several new processes are being developed for the production of urea (2). Each of these, however, is concerned with the solution production stage, not the solidification stage. Since water effluents arise from the evaporation of excess water in the solidification stage, the impact of these new processes on effluent quality is minimal.

Nitric Acid

Improvements in the basic nitric acid process previously described lie in the area of catalysts. Costs of the standard platinum catalyst are high, and efforts are always underway to recover as much as possible or to develop alternate, cheaper catalysts (23). These process changes have little or no effect on water effluent quality.

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(43) Personal communication with J. C. Barber, Tennessee Valley Authority, Muscle Shoals, Alabama, June 1976.

(44) Personal communication with J. H. Mayes, Gulf South Research Institute, Baton Rouge, Louisiana, July 1976.

(45) Sloan, C. R., and A. S. McHone. The Effect of the Energy Crisis on Ammonia Producers. In: Ammonia Plant Safety, Volume 15, Chemical Engineering Progress Technical Manual. American Institute of Chemical Engineers, New York, New York, 1973. pp. 91-95.

(46) Ammonia Plants Seek Routes to Better Gas Mileage. Chemical Week, 116(8):29, 1975.

(47) Strelzoff, S. Make Ammonia from Coal. Hydrocarbon Processing, 53(10):133-135, 1974.

INDUSTRY GROWTH TRENDS

The growth rate of the nitrogen fertilizer industry is shown in Figure 20 (1-3, 48-51). The growth in production of ammonium nitrate, ammonia, and nitric acid has been fairly level in recent years and in current projections to 1980. Urea, on the other hand, has experienced dramatic increases in recent years and has a projected growth of almost 1.5 times 1976 production for 1980. This growth is the result of use of urea in nonfertilizer areas, in forest fertilization, and in increased export of prilled urea.

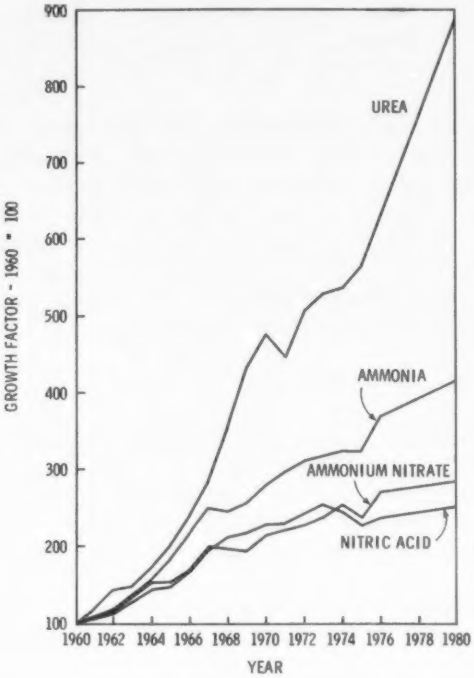

Figure 20. Growth factors for nitrogen-based fertilizers.

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(48) Current Industrial Reports, Inorganic Chemicals. U.S. Department of Commerce, Washington, D.C. M28A(72)-14, December 1972. p. 14.

(49) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products. M28B(75)-4, U.S. Department of Commerce, Washington, D.C., June 1975. p. 1.

(50) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products. M28B(76)-1, U.S. Department of Commerce, Washington, D.C., March 1976. p. 1.

(51) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products. M28B(77)-1, U.S. Department of Commerce, Washington, D.C., March 1977. p. 1.

The respective annual growth rate for each of the industries based on actual and predicted production for 1975 through 1980 is as follows:

Ammonia	5.2%
Ammonium nitrate	3.8%
Urea	9.7%
Nitric acid	1.0%

A significant factor influencing the growth of the fertilizer industry is economics. The fertilizer industry is capital intensive; therefore any expansions or new plants are affected by the supply of capital. Also, the industry is highly depenedent on the customer. It is therefore subject to seasonal demand, cyclic oversupply, "commodity type" sales price, and customer's ability to purchase. All of these factors combine to inhibit or accelerate the growth of nitrogen fertilizers.

POTENTIAL IMPACT OF CONTROLS

In the ammonia industry, the potential impact of increased utilization of controls is not too large. Already the condensate stripper, used in virtually all ammonia plants, reduces contaminants to acceptable levels. Therefore the growth of pollutants is expected to parallel the growth of the industry.

Both urea and ammonium nitrate production could possibly increase the use of already existing controls to reduce the growth of pollutants.

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APPENDIX A

RAW DATA

Plant parameters and data on receiving streams that were used in this report are compiled in Appendix A. Table A-1 gives a listing of nitrogen fertilizer plants, plant locations, and plant capacities. Tables A-2 and A-3 present data on the receiving streams into which plants discharge. In most cases receiving streams were identified by using an atlas to locate the river closest to a plant site. However, because smaller streams were not given in the atlas, and because some plants may discharge to municipal treatment systems, the listing of rivers in these tables may not be completely accurate.

TABLE A-1. NITROGEN FERTILIZER PLANTS, LOCATIONS, AND CAPACITIES

Company	City/state	Annual capacity, 10^3 metric tons		
		Ammonia	Ammonium nitrate	Urea
Agway, Inc.	Olean, NY		64	
Air Products and Chemicals, Inc.	New Orleans, LA	190		
	Pensacola, FL	68	182	21
Allied Chemical Corp.	Geismar, LA	308	102	222
	Hopewell, VA	308		
	South Point, OH	290		63
	Omaha, NE	180	272	127
American Cyanamid Co.	Hannibal, MO		123	
	New Orleans, LA	308		132
Apache Powder Co.	Benson, AZ	14		
Beker Industries, Inc.	Conda, ID	127		
	Carlsbad, NM	190		145
Borden, Inc.	Geismar, LA	258		200
California Oil Purification Co.	Ventura, CA			120
Camex, Inc.	Borger, TX	363		
CF Industries, Inc.	Donaldsonville, LA	616		329
	Fremont, NE	43	30	16
	Terre Haute, IN	122	141	
	Tyner, TN	149	116	30
	Tunis, NC	190	363	150
	Olean, NY			68
Cherokee Nitrogen Co. (N-ReN Corp.)	Pryor, OK		77	16
	Plainview, TX			41
Coastal States Gas Corp.	Cheyenne, WY	166	73	
Columbia Nitrogen Corp.	Augusta, GA	118	212	35
Cominco American, Inc.	Beatrice, NE		154	
Commercial Solvents Corp.	Sterlington, LA	308	-	
Diamond Shamrock Corp.	Dumas, TX	145		
Dow Chemical Co.	Freeport, TX	104		
DuPont Co.	Beaumont, TX	308		
	Belle, WV	308		
	Gibbstown, NJ		45	
	Seneca, IL		182	
	Victoria, TX	90		
El Paso Natural Gas Co.	Odessa, TX	104		
Ensearch Corp., Nipak, (subsidiary) (Lone Star Gas Co.)	Kerens, TX	113	65	63
	Pryor, OK	95		170
Esmark, Inc.	Beaumont, TX			45
FMC Corp.	South Charleston, WV	22		
Farmers National Chemical Co.	Plainview, TX	54		
Farmland Industries, Inc. Cooperative Farm Chemicals Assoc. (CFCA)	Dodge City, KS	181	73	58
	Lawrence, KS	308	417	244
	Ft. Dodge, IA	18		
	Hastings, NE	127		
	Enid, OK	362		
	Plainview, TX	24		
Felmont Oil Corp.	Olean, NY	77		
First Mississippi Corp.	Ft. Madison, IA	308		
Gardinier, Inc.	Tampa, FL	118		
	Helena, AR		95	61
General American Oil of Texas	Pasadena, TX			85
Goodpasture, Inc.	Dimmitt, TX	77	30	21
W. R. Grace & Co.	Wilmington, NC		197	
	Memphis, TN	300		442
	Big Spring, TX	113		
Green Valley Chemical Corp.	Creston, IA	32		
Gulf Oil Corp.	Donaldsonville, LA	308		
	Pittsburg, KS		326	
Gulf and Western Industries, Inc.	Palmerton, PA	36		
Hercules, Inc.	Bessemer, AL		23	
	Carthage, MO	-	-	-
	Donora, PA		136	
	Hercules, CA	63	73	36
	Louisiana, MO	63	459	86

Note.—Blanks indicate that the product is not produced and dashes indicate that the amount produced is unknown.

TABLE A-1 (continued)

Company	City/state	Annual capacity, 10^3 metric tons		
		Ammonia	Ammonium nitrate	Urea
Hooker Chemical Corp.	Tacoma, WA	20		
IMC Corp.	Sterlington, LA		170	
Illinois Nitrogen Co.	Marseilles, IL		136	
Kaiser Aluminum & Chemicals Corp.	Bainbridge, GA		55	
	North Bend, OH		93	
	Savannah, GA	136	229	73
	Tampa, FL		50	
Mississippi Chemical Corp.	Pascagoula, MS	159		
	Yazoo City, MS	358	708	127
Mobil Oil Corp.	Beaumont, TX	236	177	
Monsanto Co.	Luling, LA	408	322	
	El Dorado, AR		254	
Nitram, Inc.	Tampa, FL		136	
Occidental Petroleum Corp.	Lathrop, CA	87		
	Plainview, TX	47		
	Hanford, CA		33	
Olin	Lake Charles, LA	435		150
PPG Industries, Inc.	New Martinsville, WV	45		
Pennwalt Chemicals Corp.	Portland, OR	8		
Phillips Pacific Chemical Co.	Finley (Kennewick), WA	141	50	34
Phillips Petroleum Co.	Beatrice, NE	190	64	45
	Pasadena, TX	209		
	Etter, TX		168	
Reichhold Chemical, Inc.	St. Helens, OR	81	23	62
Rohm and Haas Co.	Deer Park, TX	45		
St. Paul Ammonia Products, Inc.	E. Dubuque, IL	190		77
	St. Paul, MN		208	
J. R. Simplot Co.	Pocatello, ID	100	18	14
Standard Oil of California Chevron Chem. Co., (subsidiary)	Fort Madison, IA	95	77	
	El Segundo, CA	12		
	Richmond, CA	118		
	Kennewick, WA		95	
Standard Oil of Indiana	Texas City, TX	655		
Standard Oil of Kentucky	Pascagoula, MS	463		
Standard Oil Co. of Ohio (Vistron Corp.) Solar Nitrogen Chemicals, Inc.	Lima, OH	522	58	200
	Joplin, MO	23		
Skelly Oil Co. Hawkeye Chemical Co., (subsidiary)	Clinton, IA	123	136	55
Tenneco, Inc.	Houston, TX	190		
TVA	Muscle Shoals, AL	81	39	55
Terra Chemicals International, Inc.	Sioux City, IA (Port Neal)	190	136	145
Tipperary Corp.	Lovington, NM	90		
Triad Chemical	Donaldsonville, LA	345		426
Tyler Corp. (Atlas Powder Co.)	Joplin, MO		146	67
	Tamaque, PA		14	
Union Oil Co. of California Collier Carbon & Chemical Corp., (subsidiary)	Brea, CA	236	55	109
	Kenai, AK	463		308
United States Steel Corp. USS Agri-Chemicals	Cherokee, AL	160	91	23
	Crystal City, MO		91	
	Geneva, UT	63	91	
	Clairton, PA	363		
Valley Nitrogen Producers, Inc.	El Centro, CA	190	41	17
	Helm, CA	160	69	53
	Chandler, AZ	32		
Vulcan Materials Co.	Wichita, KS	36		
The Williams Companies (Agrico Chemicals)	Henderson, KY		91	
	Verdigris, OK		239	190
	Donaldsonville, LA	308		181
	Tulsa, OK	386		
	Blytheville, AR	308		299

Note.—Blanks indicate that the product is not produced.

TABLE A-2. NITROGEN FERTILIZER PLANTS, LOCATIONS, AND WASTEWATER RECEIVING BODIES

Company	City/state	Receiving body	Flow,[a] m³/s Max	Min	Mean	Measuring station location	Reference
Agway, Inc.	Olean, NY	Allegheny River	711	5	90	Salamanca, NY	52
Air Products and Chemicals, Inc.	New Orleans, LA	Mississippi River	33,131[b]	5,925[b]	17,896[b]	Talbert Landing, MS (below Vicksburg)	53
	Pensacola, FL	Pensacola Bay					
Allied Chemical Corp.	Geismar, LA	Mississippi River	33,131[b]	5,925[b]	17,896[b]	Talbert Landing, MS	53
	Hopewell, VA	James River	3,540	32	246	Near Richmond, VA	54
	South Point, OH	Ohio River	11,300	303	3,210	Greenup Dam, KY	55
	Omaha, NE	Missouri River	2,060	317	1,190	Nebraska City, NE	56
American Cyanamid Co.	Hannibal, MO	Mississippi River	9,460	844	3,310	Alton, IL	57
	New Orleans, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
Apache Powder Co.	Benson, AZ	San Pedro River	57	0[c]	0.5	Near Benson, AZ	58
Beker Industries, Inc.	Conda, ID	Bear River	43	4.5	21	Soda Springs, ID	59
	Carlsbad, NM	Pecos River	300	0.02	3	Below Dark Canyon at Carlsbad, NM	60
Borden, Inc.	Geismar, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
California Oil Purification Co.	Ventura, CA	Pacific Ocean					
Camex, Inc.	Borger, TX	Canadian River	26	0.01	1.7	Near Canadian, TX	61
CF Industries, Inc.	Donaldsonville, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
	Fremont, NE	Platte River	–[d]	–[d]	–[d]		
	Terre Haute, IN	Wabash River	1,410	76.5	377	Terre Haute, IN	62
	Tyner, TN	Tennessee River	4,050	377	1,305	Chattanooga, TN	63
	Tunis, NC	Chowan River	–[d]	–[d]	–[d]		
	Olean, NY	Allegheny River	710	5	90	Salamanca, NY	52
Cherokee Nitrogen Co. (N-ReN Corp.)	Pryor, OK	Neosho River	–[e]	–[e]	–[e]		
	Plainview, TX	Running Water Draw	0.48	0[c]	0.02	Plainview, TX	64
Coastal States Gas Corp.	Cheyenne, WY	Crow River	7.6	0.05	0.68	Near Tipperary, WY	65
Columbia Nitrogen Corp.	Augusta, GA	Savannah River	1,243	156	331	Augusta, GA	66
Cominco American, Inc.	Beatrice, NE	Big Blue River	–[d]	–[d]	–[d]		
Commercial Solvents Corp.	Sterlington, LA	Ouachita River	1,890[b]	71[b]	1,020[b]	Monroe, LA	53
Diamond Shamrock Corp.	Dumas, TX	South Palo Duru River	63.2	0[c]	0.50	Near Spearman, TX	61
Dow Chemical Co.	Freeport, TX	Brazos River	1,725	47	397	Near Rosharon, TX	62
DuPont Co.	Beaumont, TX	Neches River	560	50	280	Evadale, TX	61
	Belle, WV	Kanawah River	3,200	67	562	Charleston, WV	69
	DuPont, WA	Sequalitchen Creek	–[d]	–[d]	–[d]		
	Gibbstown, NJ	Delaware River	–[d]	–[d]	–[d]		
	Louviers, CO	South Platte River	44	2.6	11	South Platte, CO	67
	Seneca, IL	Illinois River	1,286	81	317	Marseilles, IL	57
	Victoria, TX	Guadalupe River	821	32	99	Victoria, TX	68

See footnotes at end of table, p. 73.

TABLE A-2 (continued)

Company	City/state	Receiving body	Flow,[a] m³/s Max	Min	Mean	Measuring station location	Reference
El Paso Natural Gas Co.	Odessa, TX	Johnson River	–[d]	–[d]	–[d]		
Ensearch Corp., Nipak, subsidiary	Kerens, TX	Chambers River	634	0.02	28	Near Corsicana, TX	61
(Lone Star Gas Co.)	Pryor, OK	Neosho River	–[f]	–[f]	–[f]		
Esmark, Inc.	Beaumont, TX	Neches River	560	50	280	Evadale, TX	61
FMC Corp.	South Charleston, WV	Kanawha River	3,200	67	562	Charleston, WV	69
Farmers National Chemical Co.	Plainview, TX	Running Water Draw	0.48	0[c]	0.02	Plainview, TX	64
Farmland Industries, Inc.	Dodge City, KS	Arkansas River	1.6	0	0.35	Dodge City, KS	70
Cooperative Farm Chemicals	Lawrence, KS	Kansas River	1,360	50	177	Desoto, KS	70
Association (CFCA)	Fort Dodge, IA	Des Moines River	334	2	38	Fort Dodge, IA	71
	Hastings, NE	–[g]					
	Enid, OK	Turkey River	–[f]	–[f]	–[f]		
	Plainview, TX	Running Water Draw	0.48	0	0.02	Plainview, TX	64
Felmont Oil Corp.	Olean, NY	Allegheny River	710	5	90	Salamanca, NY	52
First Mississippi Corp.	Fort Madison, IA	Mississippi River	7,140	637	2,100	Keokuk, IA	71
Gardinier, Inc.	Tampa, FL	Tampa Bay					
	Helena, AR	Mississippi River	42,200[b]	6,400[b]	19,930[b]	Memphis, TN	63
General American Oil of Texas	Pasadena, TX	Houston Ship Channel	–[d]	–[d]	–[d]		
Goodpasture, Inc.	Dimmitt, TX	–[g]					
W. R. Grace & Co.	Wilmington, NC	Atlantic Ocean					
	Memphis, TN	Mississippi River	42,200	6,400	19,930	Memphis, TN	63
	Big Spring, TX	Beals Creek	5.2	0	0.3	Above Big Spring, TX	68
Green Valley Chemical Corp.	Creston, IA	Platte River	66	0.03	2.2	Near Diagonal, IA	71
Gulf Oil Corp.	Donaldsonville, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
	Pittsburg, KS	–[g]					
Gulf and Western Industries, Inc.	Palmerton, PA	Lehigh River	310	14	64	Walnutport, PA	72
Hercules, Inc.	Bessemer, AL	–[g]					
	Carthage, MO	Spring River	170	3	18	Carthage, MO	73
	Donora, PA	Monongahela River	2,165	20	314	Charleroi, PA	74
	Hercules, CA	San Francisco Bay					
	Louisiana, MO	Mississippi River	9,460	844	3,305	Alton, IL	57
Hooker Chemical Corp.	Tacoma, WA	Puyallup River	785	15	103	Payallup, WA	75
IMC Corp.	Sterlington, LA	Ouachita River	1,890[b]	71[b]	1,020[b]	Monroe, LA	53
Illinois Nitrogen Co.	Marseilles, IL	Illinois River	1,286	81	317	Marseilles, IL	57

See footnotes at end of table, p. 73.

TABLE A-2 (continued)

Company	City/state	Receiving body	Flow,[a] m³/s Max	 Min	 Mean	Measuring station location	Reference
Kaiser Aluminum & Chemicals Corp.	Bainbridge, GA	Flint River	0.76	0.50	0.57	Bainbridge, GA	66
	North Bend, OH	Dark Hollow Run	–[f]	–[f]	–[f]		
	Savannah, GA	Pipemaker Canal	–[f]	–[f]	–[f]		
	Tampa, FL	Sixmile River	–[f]	–[f]	–[f]		
Mississippi Chemical Corp.	Pascagoula, MS	Gulf of Mexico					
	Yazoo City, MS	Martin Creek	–[f]	–[f]	–[f]		
Mobil Oil Corp.	Beaumont, TX	Neches River	561	50	281	Evadale, TX	61
Monsanto Co.	Luling, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
	El Dorado, AR	Ouachita River	–[d]	–[d]	–[d]		
Nitram, Inc.	Tampa, FL	Hillsborough River	–[f]	–[f]	–[f]		
Occidental Petroleum Corp.	Lathrop, CA	San Joaquin River	250	38	110	Near Vernalis, CA	76
	Plainview, TX	Running Water Draw	0.48	0[c]	0.02	Plainview, TX	64
	Hanford, CA	Lakeland Canal	–[d]	–[d]	–[d]		
Olin	Lake Charles, LA	Beckwith River	68	0.13	8	Near DeQuincy, LA	53
PPG Industries, Inc.	New Martinsville, WV	Ohio River	9,460	156	1,966	Belleville Dam, WV	69
Pennwalt Chemicals Corp.	Portland, OR	Willamette River	3,400	175	994	Portland, OR	77
Phillips Pacific Chemical Co.	Finley (Kennewick), WA	Columbia River	6,004	1,240	3,350	Below Priest Rapids Dam, WA	75
Phillips Petroleum Co.	Beatrice, NE	Big Blue River	–[d]	–[d]	–[d]		
	Pasadena, TX	Houston Ship Channel					
	Etter, TX	South Palo Duru	63	0	0.50	Near Spearman, TX	61
Reichhold Chemical, Inc.	St. Helens, OR	Columbia, River	–[d]	–[d]	–[d]		
Rohm and Haas Co.	Deer Park, TX	Galveston Bay					
St. Paul Ammonia Products, Inc.	East Dubuque, IL	Mississippi River	6,060	518	1,420	Clinton, IA	71
	St. Paul, MN	Mississippi River	2,212	41	415	St. Paul, MN	78
J. R. Simplot Co.	Pocatello, ID	Portneuf River	43	3.6	13	Pocatello, ID	59
Standard Oil of California	Fort Madison, IA	Mississippi River	7,140	637	2,100	Keokuk, IA	71
Chevron Chemical Co. (subsidiary)	El Segundo, CA	Pacific Ocean					
	Richmond, CA	Pacific Ocean					
	Kennewick, WA	Columbia River	6,000	1,240	3,350	Below Priest Rapids Dam, WA	75
Standard Oil of Indiana	Texas City, TX	Gulf of Mexico					
Standard Oil of Kentucky	Pascagoula, MS	Gulf of Mexico					
Standard Oil Co. of Ohio (Vistron Corp.)	Lima, OH	Ottawa River	115	0.5	4	Allentown, OH	79
Solar Nitrogen Chemicals, Inc.	Joplin, MO	Shoal River	414	4	20	Above Joplin, MO	73

See footnotes at end of table, p. 73.

TABLE A-2 (continued)

Company	City/state	Receiving body	Flow,[a] m^3/s Max	Min	Mean	Measuring station location	Reference
Skelly Oil Co. Hawkeye Chemical Co. (subsidiary)	Clinton, IA	Mississippi River	6,060	518	1,420	Clinton, IA	71
Tenneco, Inc.	Houston, TX	Houston Ship Channel	–[d]	–[d]	–[d]		
TVA	Muscle Shoals, AL	Tennessee River	8,694	498	1,986	Florence, AL	80
Terra Chemicals International, Inc.	Sioux City, IA (Port Neal)	Missouri River	1,818	227	1,005	Sioux City, IA	71
Tipperary Corp.	Lovington, NM	–[g]					
Triad Chemical	Donaldsonville, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
Tyler Corp. (Atlas Powder Co.)	Joplin, MO	Shoal River	414	4	20	Above Joplin, MO	73
	Tamaque, PA	Schuylkill River	31	0.5	3	Tamaque, PA	72
Union Oil Co. of California Collier Carbon & Chemical Corp. (subsidiary)	Brea, CA	–[h]					
	Kenai, AK	Cook Inlet					
United States Steel Corp. USS Agri-Chemicals	Cherokee, AL	Tennessee River	8,694	498	1,986	Florence, AL	80
	Crystal City, MO	Mississippi River	–[d]	–[d]	–[d]		
	Geneva, UT	–[e]					
	Clairton, PA	–[e]					
Valley Nitrogen Producers, Inc.	El Centro, CA	Alamo River	48	14	26	Near Niland, CA	81
	Helm, CA	Fresno Slough	–[d]	–[d]	–[d]		
	Chandler, AZ	–[g]					
Vulcan Materials Co.	Wichita, KS	Arkansas River	300	7	29	Wichita, KS	70
The Williams Companies (Agrico Chemicals)	Henderson, KY	Ohio River	14,560	370	4,600	Louisville, KY	55
	Verdigris, OK	Verdigris River	–[f]	–[f]	–[f]		
	Donaldsonville, LA	Mississippi River	33,131[b]	5,975[b]	17,896[b]	Talbert Landing, MS	53
	Tulsa, OK	Verdigris River	–[f]	–[f]	–[f]		
	Blytheville, AR	–[g]					

[a] Maximum, minimum, and mean of daily averages for the 1975 water year (October 1974 to September 1975).

[b] Value for 1974 water year.

[c] No flow for a portion of the year.

[d] Measurements not readily available.

[e] Could not locate city on road atlas.

[f] Water Resources Data not available in microfiche file.

[g] No river noted within a 16.1-km (10-mi) radius of city.

[h] Discharge into an underground sewer line which connects to a large sanitation district central treating plant.

TABLE A-3. NITROGEN FERTILIZER PLANTS AND RECEIVING STREAM PARAMETERS[a]

Company	City/state	Receiving body	pH, Max	pH, Min	pH, Mean	Water temperature, °C Max	Water temperature, °C Min	Water temperature, °C Mean
Agway, Inc.	Olean, NY	Allegheny River						
Air Products and Chemicals, Inc.	New Orleans, LA	Mississippi River						
	Pensacola, FL	Pensacola Bay						
Allied Chemical Corp.	Geismar, LA	Mississippi River						
	Hopewell, VA	James River						
	South Point, OH	Ohio River	7.6	6.8	7.2	28.0	4.5	15.9
	Omaha, NE	Missouri River						
American Cyanamid Co.	Hannibal, MO	Mississippi River				30.0	0	
	New Orleans, LA	Mississippi River						
Apache Powder Co.	Benson, AZ	San Pedro River						
Beker Industries, Inc.	Conda, ID	Bear River				18.0	7.5	12.9
	Carlsbad, NM	Pecos River						
Borden, Inc.	Geismar, LA	Mississippi River						
California Oil Purification Co.	Ventura, CA	Pacific Ocean						
Camex, Inc.	Borger, TX	Canadian River	8.5	7.5	8.1	32.0	2.0	15.3
CF Industries, Inc. (Central Farmers Fertilizer Co.)	Donaldsonville, LA	Mississippi River						
	Fremont, NE	Platte River						
	Terre Haute, IN	Wabash River						
	Tyner, TN	Tennessee River						
	Tunis, NC	Chowan River						
	Olean, NY	Allegheny River						
Cherokee Nitrogen Co. (N-ReN Corp.)	Pryor, OK	Neosho River						
	Plainview, TX	Running Water Draw						
Coastal States Gas Corp.	Cheyenne, WY	Crow River						
Columbia Nitrogen Corp.	Augusta, GA	Savannah River						
Cominco American, Inc.	Beatrice, NE	Big Blue River						
Commercial Solvents Corp.	Sterlington, LA	Ouachita River	7.0	6.2	6.6	29.0	8.0	19.0
Diamond Shamrock Corp.	Dumas, TX	South Palo Duru River	8.5	7.6	7.9	25.0	15.0	20.0
Dow Chemical Co.	Freeport, TX	Brazos River	7.9	6.3	7.0	29.0	10.0	20.8
DuPont Co.	Beaumont, TX	Neches River	7.1	6.3	6.7	29.5	11.0	20.4
	Belle, WV	Kanawah River				33.0	4.0	
	DuPont, WA	Sequalitchen Creek						
	Gibbstown, NJ	Delaware River						
	Louviers, CO	South Platte River						
	Seneca, IL	Illinois River	7.9	7.1	7.5	30.0	4.0	15.5
	Victoria, TX	Guadalupe River	8.0	7.7	7.8	30.0	14.0	22.9

See footnotes at end of table, p. 77.

TABLE A-3 (continued)

Company	City/state	Receiving body	pH, Max	pH, Min	pH, Mean	Water temperature, °C Max	Water temperature, °C Min	Water temperature, °C Mean
El Paso Natural Gas Co.	Odessa, TX	Johnson River						
Ensearch Corp., Nipak, subsidiary (Lone Star Gas Co.)	Kerens, TX	Chambers River	8.3	7.4	7.8	27.5	7.0	18.6
	Pryor, OK	Neosho River						
Esmark, Inc.	Beaumont, TX	Neches River	7.1	6.3	6.7	29.5	11.0	20.4
FMC Corp.	South Charleston, WV	Kanawha River				33.0	4.0	
Farmers National Chemical Co.	Plainview, TX	Running Water Draw						
Farmland Industries, Inc. Cooperative Farm Chemicals Association (CFCA)	Dodge City, KS	Arkansas River	8.7	7.0	7.9	32.0	0.5	14.8
	Lawrence, KS	Kansas River	8.6	7.9	8.2	25.0	1.5	14.9
	Fort Dodge, IA	Des Moines River						
	Hastings, NE	–[b]						
	Enid, OK	Turkey River						
	Plainview, TX	Running Water Draw						
Felmont Oil Corp.	Olean, NY	Allegheny River						
First Mississippi Corp.	Fort Madison, IA	Mississippi River	8.6	7.8	8.4	30.0	0	15.9
Gardinier, Inc.	Tampa, FL	Tampa Bay						
	Helena, AR	Mississippi River						
General American Oil of Texas	Pasadena, TX	Houston Ship Channel						
Goodpasture, Inc.	Dimmitt, TX	–[b]						
W. R. Grace & Co.	Wilmington, NC	Atlantic Ocean						
	Memphis, TN	Mississippi River						
	Big Spring, TX	Beals Creek	8.2	6.9	7.5	25.5	5.0	17.5
Green Valley Chemical Corp.	Creston, IA	Platte River						
Gulf Oil Corp.	Donaldsonville, LA	Mississippi River						
	Pittsburg, KS	–[b]						
Hercules, Inc.	Bessemer, AL	–[b]						
	Carthage, MO	Spring River						
	Donora, PA	Monongahela River						
	Hercules, CA	San Francisco Bay						
	Louisiana, MO	Mississippi River				30.0	0	
Hooker Chemical Corp.	Tacoma, WA	Puyallup River	7.6	6.9	7.3	16.3	3.4	10.0
IMC Corp.	Sterlington, LA	Ouachita River	7.0	6.2	6.6	29.0	8.0	19.0
Illinois Nitrogen Co.	Marseilles, IL	Illinois River	7.9	7.1	7.5	30.0	4.0	15.5

See footnotes at end of table, p. 77.

TABLE A-3 (continued)

Company	City/state	Receiving body	pH, Max	pH, Min	pH, Mean	Water temperature, °C Max	Water temperature, °C Min	Water temperature, °C Mean
Kaiser Aluminum & Chemicals Corp.	Bainbridge, GA	Flint River						
	North Bend, OH	Dark Hollow Run						
	Savannah, GA	Pipemaker Canal						
	Tampa, FL	Sixmile River						
Mississippi Chemical Corp.	Pascagoula, MS	Gulf of Mexico						
	Yazoo City, MS	Martin Creek						
Mobil Oil Corp.	Beaumont, TX	Neches River	7.1	6.3	6.7	29.5	11.0	20.4
Monsanto Co.	Luling, LA	Mississippi River						
	El Dorado, AR	Ouachita River						
Nitram, Inc.	Tampa, FL	Hillsborough River						
Occidental Petroleum Corp.	Lathrop, CA	San Joaquin River	8.3	7.4	7.9	23.5	10.5	15.8
	Plainview, TX	Running Water Draw						
	Hanford, CA	Lakeland Canal						
Olin	Lake Charles, LA	Beckwith River						
Pennwalt Chemicals Corp.	Portland, OR	Willamette River	8.5	7.0	7.9	20.1	5.5	11.7
Phillips Pacific Chemical Co.	Finley (Kennewick), WA	Columbia River						
Phillips Petroleum Co.	Beatrice, NE	Big Blue River						
	Pasadena, TX	Houston Ship Channel						
	Etter, TX	South Palo Duru						
Reichhold Chemical, Inc.	St. Helens, OR	Columbia, River						
Rohm and Haas Co.	Deer Park, TX	Galveston Bay						
St. Paul Ammonia Products, Inc.	East Dubuque, IL	Mississippi River	8.8	7.8	8.5	29.0	0	13.6
	St. Paul, MN	Mississippi River	8.6	7.9	8.2	25.5	0.5	10.5
J. R. Simplot Co.	Pocatello, ID	Portneuf River				20.0	1.0	8.1
Standard Oil of California Chevron Chemical Co. (subsidiary)	Fort Madison, IA	Mississippi River	8.6	7.8	8.4	30.0	0	15.9
	El Segundo, CA	Pacific Ocean						
	Richmond, CA	Pacific Ocean						
	Kennewick, WA	Columbia River						
Standard Oil of Indiana	Texas City, TX	Gulf of Mexico						
Standard Oil of Kentucky	Pascagoula, MS	Gulf of Mexico						
Standard Oil Co. of Ohio (Vistron Corp.)	Lima, OH	Ottawa River						
Solar Nitrogen Chemicals, Inc.	Joplin, MO	Shoal River						

See footnotes at end of table, p. 77.

TABLE A-3 (continued)

Company	City/state	Receiving body	pH, Max	pH, Min	pH, Mean	Water temperature, °C[a] Max	Water temperature, °C Min	Water temperature, °C Mean
Skelly Oil Co. Hawkeye Chemical Co. (subsidiary)	Clinton, IA	Mississippi River	8.8	7.8	8.5	29.0	0	13.6
Tenneco, Inc.	Houston, TX	Houston Ship Channel						
TVA	Muscle Shoals, AL	Tennessee River	7.8	6.9	7.4	28.0	7.5	17.3
Terra Chemicals International, Inc.	Sioux City, IA (Port Neal)	Missouri River	8.8	7.6	8.1	26.0	0	9.3
Tipperary Corp.	Lovington, NM	–[b]						
Triad Chemical	Donaldsonville, LA	Mississippi River						
Tyler Corp (Atlas Powder Co.)	Joplin, MO	Shoal River						
	Tamaque, PA	Schuylkill River						
Union Oil Co. of California Collier Carbon & Chemical Corp. (subsidiary)	Brea, CA	–[c]						
	Kenai, AK	Cook Inlet						
United States Steel Corp. USS Agri-Chemicals	Cherokee, AL	Tennessee River	7.8	6.9	7.4	28.0	7.5	17.3
	Crystal City, MO	Mississippi River						
	Geneva, UT	–[d]						
	Clairton, PA	–[d]						
Valley Nitrogen Producers, Inc.	El Centro, CA	Alamo River						
	Helm, CA	Fresno Slough						
	Chandler, AZ	–[b]						
Vulcan Materials Co.	Wichita, KS	Arkansas River						
The Williams Companies (Agrico Chemicals)	Henderson, KY	Ohio River						
	Verdigris, OK	Verdigris River						
	Donaldsonville, LA	Mississippi River						
	Tulsa, OK	Verdigris River						
	Blytheville, AR	–[b]						

[a] Blanks indicate data not available.

[b] No river noted within a 16.1-km (10-mi) radius of city.

[c] Discharge into an underground sewer line which connects to a large sanitation district central treating plant.

[d] Could not locate city on road atlas.

APPENDIX B

CALCULATION OF EFFLUENT PARAMETERS

Effluent parameters used to characterize wastewater streams from the production of ammonium nitrate and urea were calculated from data supplied to the EPA by industry. A cross section of companies producing ammonium nitrate and/or urea responded to an EPA request for effluent data to enable them to formulate meaningful effluent guidelines for the nitrogen fertilizer industry. The data received were compiled and are listed in Tables B-1 and B-2.[a] Table B-1 presents compiled data characterizing effluents from ammonium nitrate production, while Table B-2 presents compiled data characterizing effluents from urea production.

Difficulties occurred in reducing the original data to a form useful in calculating source severities. The original data provided to EPA were often incomplete. Generally, data characterized the total discharge from an entire nitrogen fertilizer plant, thus combining discharges from ammonium nitrate, urea, ammonia, and nitric acid production. The nature of the nitrogen fertilizer plants sampled and sampling techniques used varied drastically. In addition, observed variations in discharge characteristics could be attributed to variations in the:

- Size of the nitrogen fertilizer plants.
- Age of the nitrogen fertilizer plants.
- Configuration of the plants (location of nitric acid and ammonia plant in the sewerage system).
- Type of cooling systems used: closed loop or single pass.
- Type of product: prilled or solution.
- Techniques of handling process off-gases: condensing or venting.
- Plant maintenance procedures.
- Occurrence of significant spills while effluent sampling was conducted.
- Inclusion of land surrounding the nitrogen fertilizer plant in the sewage system leading to the final discharge.

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[a] Data on file at the Effluent Guidelines Division, U.S. Environmental Protection Agency, Washington, D.C., 1977.

TABLE B-1. LISTING OF COMPILED RAW DATA CHARACTERIZING THE WASTEWATER STREAMS FROM AMMONIUM NITRATE PLANTS

Plant	Product	Production, metric ton/day	Wastewater flow, m^3/s	Wastewater flow/product produced, m^3/metric ton	Nitrogen g/metric ton		Nitrogen g/day		Nitrogen concentration, g/m^3		Receiving water flow, m^3/s	
					NH^3-N	NO^{3-}-N	NH^3-N	NO^{3-}-N	NH^3-N	NO^{3-}-N	1-yr Low	1-yr Mean
$A^{a,b}$	P(55%)-S	717	6.8×10^{-3}	0.82	10	12	7,170	8,604	<0.1	<0.1	NA[c]	NA
B	P(56%)-S	1,004	1.95×10^{-3}	0.17	11	12	11,044	12,048	65	72	377	1,305
D^d	P(75%)-S	204	5×10^{-4}	0.21	585	120	119,340	24,480	2,760	567	NA	NA
E^a	S	67	3.2×10^{-3}	4.13	75	66	5,025	4,422	18.2	16.1	NA	NA
G^a	S	155	1.211×10^{-1}	67.5	1,200	251	186,000	38,905	17.8	3.7	5	90
H^d	S	194	9×10^{-4}	0.40	3,652	381	708,488	73,914	9,111	951	0.05	0.68
I	S	160	2.86×10^{-2}	15.4	2,173	1,434	347,680	229,440	141	92.9	0.5	4
$J^{a,d}$	P(45%)-S	914	2.63×10^{-2}	2.49	207	178	188,784	162,692	83.1	71.6	205	448
K^a	S	61	2.437×10^{-1}	345	70	379	4,270	23,119	0.2	1.1	NA	NA
M	P(85%)-S	1,111	1.13×10^{-3}	0.09	185	255	205,535	283,304	2,110	2,900	50	177
$N^{a,b}$	P(56%)-S	360	7×10^{-4}	0.17	7	6	2,520	2,160	0.1	0.1	518	1,420
P^a	P(34%)-S	390	2.05×10^{-2}	4.54	1,038	110	404,820	42,900	229	24.2	227	1,005
Q^a	P	295	1.414×10^{-1}	41.4	1,880	346	554,600	102,070	45.4	8.4	NA	NA
R	S	286	2.52×10^{-1}	76.1	1,330	1,450	380,380	414,700	17.5	19.0	317	1,190
S^a	S	804	8.40×10^{-2}	9.03	2,630	680	2,114,520	546,720	291	75.3	5,975	17,896
T^d	P(75%)-S	283	3.4×10^{-3}	1.04	5,400	810	1,528,200	229,230	5,200	780	498	1,986
$U^{a,b}$	P(50%)-S	531	5.07×10^{-2}	8.24	1,230	737	653,130	391,347	149	89	156	331
V^a	P(60%)-S	242	5.91×10^{-2}	21.1	10,440	3,130	2,526,480	757,460	495	148	6,400	19,930
W^d	P	411	4.71×10^{-2}	9.90	1,080	1,940	443,880	797,340	109	196	NA	NA
X	Solid (90%)-S	309	3.2×10^{-2}	8.95	1,900	1,500	587,100	463,500	212	168	71	1,020
Y^d	S	147	2.1×10^{-3}	1.23	947	1,125	139,209	165,375	767	911	0.50	0.57
Z	P(30%)-S	336	7.100×10^{-1}	183	895	734	300,720	246,624	4.9	4.0	81	317
AA	P^e(75%)-S^f	342	0	0	0	0	0	0	0	0	76.5	377
BB	S	241	7.7×10^{-3}	2.76	948	577	228,468	139,057	343	209	303	3,210
CC	S	133	2.2×10^{-3}	1.43	352	408	46,816	54,264	246	285	NA	NA
DD^d	P(94%)-S	401	1.44×10^{-2}	3.10	96	198	38,496	79,398	30.9	63.8	NA	NA
EE^d	P(56%)-S	560	3.4×10^{-3}	0.52	30	22	16,800	12,320	0.1	0.1	Ocean	Ocean
FF^d	P(95%)-S	654	2.74×10^{-2}	3.62	294	178	192,276	116,412	81.2	49.2	41	415
GG^d	P(86%)-S	228	2.42×10^{-2}	9.17	153	52	34,884	11,856	16.7	5.7	NA	NA
HH^d	G^g	391	6.2×10^{-3}	1.37	24	75	9,384	29,325	17.5	54.7	NA	NA

[a] Data reported as one discharge from both ammonium nitrate and urea production, proportioning method used to assign values to each process.

[b] Data reported as TKN, proportioning method used to assign appropriate values of NH_3-N and ORG-N.

[c] Not available.

[d] Summary sheets used, original data not available.

[e] Prilled.

[f] Solution.

[g] Granular.

TABLE B-2. LISTING OF COMPILED RAW DATA CHARACTERIZING WASTEWATER STREAMS FROM UREA PLANTS

Plant	Product	Production metric tons/day (as 100% urea)	Wastewater flow, m^3/s	Wastewater flow/ product produced, m^3/metric ton	Nitrogen, g/metric ton urea produced		Nitrogen g/day		Nitrogen concentration, g/m^3		Receiving water flow, m^3/s	
					NH_3-N	ORG-N	NH_3-N	ORG-N	NH_3-N	ORG-N	1-yr Low	1-Yr Mean
A[a,b]	S[c]	269	1.89×10^{-3}	0.61	8	8	2,152	2,152	13	13	NA[d]	NA
B	S	322	4.41×10^{-4}	0.12	8	NA	2,576	NA	68	NA	377	1,305
C[e]	P[f]	1,083	1.64×10^{-2}	1.30	33	22	35,739	23,826	25	17	5,975	17,896
D[e]	S	45	7×10^{-4}	1.34	152	30	6,840	1,350	113	22	NA	NA
E[a]	S	51	1.8×10^{-3}	3.05	56	39	2,856	1,989	18	13	NA	NA
F	S	161	2.4×10^{-3}	1.29	231	54	37,191	8,694	179	42	498	1,986
G[a]	P(40%)-S	191	1.108×10^{-1}	50.1	900	63	171,900	12,033	18	1	5	90
H[e]	P(75%)-S	142	1.6×10^{-3}	0.97	1,003	80	142,426	11,360	1,030	82	0.05	0.68
I	P(17%)-S	550	7.36×10^{-2}	11.6	57	129	31,350	70,950	5	11	0.5	4
J[a,e]	S	210	4.5×10^{-3}	1.85	154	193	32,340	40,530	83	104	205	448
K[a]	P(80%)-S	168	5.11×10^{-1}	263	54	224	9,072	37,632	0.2	0.9	NA	NA
L	G[g]	701	6.67×10^{-2}	8.22	501	310	351,201	217,310	61	38	5,975	17,896
M	G(70%)-S	596	7.4×10^{-3}	1.07	258	488	153,768	290,848	241	455	50	177
N	S	114	2×10^{-4}	0.15	30	552	3,420	62,928	198	3,640	518	1,420
O	P	1,000	2.63×10^{-2}	2.27	183	68	183,000	68,000	81	30	Ocean	Ocean
P[a]	P(46%)-S	494	1.93×10^{-2}	3.38	1,038	NA	512,772	NA	308	NA	227	1,005
Q[a]	P	155	5.54×10^{-2}	30.9	1,490	877	230,950	135,935	48	28	NA	NA
R	S	337	2.174×10^{-1}	55.7	5,140	960	1,732,180	323,520	92	17	317	1,190
S[a,e]	S	661	5.15×10^{-2}	6.73	1,960	110	1,295,560	72,710	291	16	5,975	17,896
T[e]	S	60	1.93×10^{-2}	27.8	6,180	4,460	370,800	267,600	222	160	498	1,986
U[a,b]	S	95	9.07×10^{-3}	83.9	920	920	87,400	87,400	112	112	156	331
V[a,e]	P(40%)-S	117	2.13×10^{-2}	15.7	7,780	18,380	910,260	2,150,460	495	1,169	6,400	19,930

[a] Data reported as one discharge from both ammonium nitrate and urea production, proportioning method used to assign values to each process.

[b] Data reported as TKN, proportioning method used to assign appropriate values of NH_3-N and ORG-N.

[c] Solution.

[d] Not available.

[e] Summary sheets used, original data not available.

[f] Prilled.

[g] Granular.

- Occurrence of precipitation while sampling was performed.
- Detention times in sewage systems (these affect extent of ammonia absorption or stripping, ammonia or urea oxidation by microorganisms in aerobic conditions, and nitrate reduction by microorganisms in anaerobic conditions).
- pH of the sewages (high pH enhances NH_3 stripping).
- Extent of water recycle in the complexes.
- Occurrence and extent of effluent treatment.

Because some of the reporting plants supplied data characterizing the total effluent from a nitrogen fertilizer complex producing both urea and ammonium nitrate, certain effluent parameters had to be segregated as those emanating from ammonium nitrate production and those emanating from urea production. An alternate solution would have been to assign all of the reported effluent parameters to both ammonium nitrate and urea production, but this would have amounted to double counting.

A series of assumptions were made in segregating the parameters to ammonium nitrate and urea production. First of all, it was assumed that nitrate nitrogen appearing in the total discharge originated entirely from ammonium nitrate production, while organic nitrogen appearing in the total discharge originated entirely from urea production. An approximation was used to segregate the wastewater flow and ammonia nitrogen discharge to urea and ammonium nitrate production. It was assumed that the amount of wastewater generated by each plant (urea or ammonium nitrate) and the amount of ammonia nitrogen discharged by each plant were roughly proportional to the amount of nitrogen (in the form of product ammonium nitrate or urea) each plant in a given nitrogen fertilizer complex produces. The following series of equations represents the stated assumptions and was used to compute the wastewater flow and ammonia nitrogen contribution from urea and ammonium nitrate production to the total discharge of the nitrogen fertilizer complex:

$$P_{AN} \times C_{AN} = PN_{AN} \tag{B-1}$$

$$P_U \times C_U = PN_U \tag{B-2}$$

$$PN_T = PN_{AN} + PN_U \tag{B-3}$$

where P_{AN} = weight of product ammonium nitrate per time, metric tons/day
P_U = weight of product urea per time, metric tons/day
C_{AN} = fraction of nitrogen in ammonium nitrate (0.47)
C_U = fraction of nitrogen in urea (0.35)

PN_{AN} = weight of product nitrogen in ammonium nitrate form per time, metric tons/day
PN_U = weight of product nitrogen in urea form per time, metric tons/day
PN_T = total weight of product nitrogen per time, metric tons/day

$$\frac{PN_{AN}}{PN_T} \times NH_3\text{-}N_T = NH_3\text{-}N_{AN} \qquad \text{(B-4)}$$

$$\frac{PN_U}{PN_T} \times NH_3\text{-}N_T = NH_3\text{-}N_U \qquad \text{(B-5)}$$

$$\frac{PN_{AN}}{PN_T} \times V_{D_T} = V_{D_{AN}} \qquad \text{(B-6)}$$

$$\frac{PN_U}{PN_T} \times V_{D_T} = V_{D_U} \qquad \text{(B-7)}$$

where $NH_3\text{-}N_T$ = total discharged ammonia nitrogen, metric tons/day
$NH_3\text{-}N_{AN}$ = ammonia nitrogen discharged from the ammonium nitrate plant, metric tons/day
$NH_3\text{-}N_U$ = ammonia nitrogen discharged from the urea plant, metric tons/day
V_{D_T} = volumetric flow rate from total plant, m^3/s
$V_{D_{AN}}$ = volumetric flow rate from ammonium nitrate plant, m^3/s
V_{D_U} = volumetric flow rate from urea plant, m^3/s m^3/s

In a few cases, nitrogen content of the discharge stream was reported in terms of total Kjeldahl nitrogen (TKN). The TKN test measures ammonia-nitrogen and organic nitrogen, but not nitrate nitrogen (82). Therefore, in order to segregate nitrogen to ammonia nitrogen and organic nitrogen in the case of urea production discharge, it was assumed that the ratio of ammonia nitrogen to organic nitrogen present in the discharge was 1:1. The following series of equations represents these stated assumptions and was used when TKN was the effluent parameter reported.

$$\frac{PN_{AN}}{PN_T} \times [(TKN) - (ORG\text{-}N_U)] = NH_3\text{-}N_{AN} \qquad \text{(B-8)}$$

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(82) Standard Methods for the Examination of Water and Wastewater. Thirteenth Edition. American Public Health Association, New York, New York, 1971. 874 pp.

$$\frac{PN_U}{PN_T} \times [(TKN) - (ORG\text{-}N_U)] = NH_3\text{-}N_U \qquad (B\text{-}9)$$

where $$NH_3\text{-}N_U = ORG\text{-}N_U \qquad (B\text{-}10)$$

TKN = total Kjeldahl nitrogen, metric tons/day
$ORG\text{-}N_U$ = organic nitrogen discharge from the urea plant, metric tons/day

The segregation of effluent characteristics in the case of a composite waste stream from a nitrogen fertilizer complex, and the segregation of TKN to ammonia nitrogen and organic nitrogen in the case of urea production, were the only modifications to the original data as submitted to the EPA. Modifications due to other effects listed previously were not made due to lack of sufficient data and desire to preserve the actual range of effluent parameters occurring within the industry.

Various statistical parameters were computed using the data listed in Tables B-1 and B-2 to derive effluent parameters representative of all urea or ammonium nitrate plants. These computed values are presented in Tables B-3 through B-6.

TABLE B-3. CALCULATED STATISTICAL PARAMETERS CHARACTERIZING WASTEWATER STREAMS FROM AMMONIUM NITRATE PLANTS

	Minimum	Maximum	Mean	Standard deviation	Median
All x_i's, nonweighted:					
Production rate, metric tons/day (as 100% ammonium nitrate)	36	1,111	386	278	309
Wastewater flow, m^3/s	0	0.71	0.063	0.136	0.021
Ratio of wastewater flow to production rate, m^3/metric ton	0	345	30.0	70.5	3.6
Waste NH_3-N:					
g nitrogen/metric ton	0	10,400	1,570	2,600	895
g nitrogen/day	0	2,530,000	398,000	604,000	192,000
Waste NO_3^--N:					
g nitrogen/metric ton	0	5,180	721	1,090	346
g nitrogen/day	0	797,000	182,000	217,000	102,000
Wastewater concentration, g nitrogen/m^3:					
NH_3-N	0	9,111	731	1,890	83.1
NO_3^--N	0	2,900	252	559	63.8
1-Yr receiving water flow, m^3/s:					
Low	0.05	6,400	805	1,905	156
Mean	0.57	19,930	2,694	5,782	448
Two extreme x_i's eliminated, nonweighted:					
Production rate, metric tons/day (as 100% ammonium nitrate)	61	1,004	373	245	309
Wastewater flow, m^3/s	0.001	0.252	0.043	0.067	0.021
Ratio of wastewater flow to production rate, m^3/metric ton	0.1	183	20.1	40.6	3.6
Waste NH_3-N:					
g nitrogen/metric ton	7	9,920	1,320	2,060	895
g nitrogen/day	2,520	2,110,000	338,000	469,000	192,000
Waste NO_3^--N:					
g nitrogen/metric ton	6	3,130	592	719	346
g nitrogen/day	2,160	758,000	167,000	189,000	102,000
Wastewater concentration, g nitrogen/m^3:					
NH_3-N	0.1	5,200	467	1,100	83.1
NO_3^--N	0.1	951	170	273	63.8
1-Yr receiving water flow, m^3/s:					
Low	0.5	5,975	524	1,415	156
Mean	4	17,896	1,839	4,220	448

TABLE B-4. CALCULATED STATISTICAL PARAMETERS CHARACTERIZING WASTEWATER STREAMS FROM UREA PLANTS

	Minimum	Maximum	Mean	Standard deviation	Median
All x_i's, nonweighted:					
Production rate, metric tons/day (as 100% ammonium nitrate)	45	1,083	342	304	201
Wastewater flow, m^3/s	0.0002	0.511	0.0554	0.1136	0.0179
Ratio of wastewater flow to production rate, m^3/metric ton	0.12	263	26.0	57.4	3.22
Waste NH_3-N:					
g nitrogen/metric ton	8	7,780	1,280	2,180	245
g nitrogen/day	2,150	1,730,000	287,000	458,000	115,000
Waste ORG-N:					
g nitrogen/metric ton	8	18,400	1,400	4,120	161
g nitrogen/day	1,350	2,150,000	190,000	473,000	51,700
Wastewater concentration, g nitrogen/m^3:					
NH_3-N	0.2	1,030	168	239	88
ORG-N	0.9	3,640	299	830	29
1-Yr receiving water flow, m^3/s:					
Low	0.05	6,400	1,698	2,621	347
Mean	4	19,930	5,227	7,896	1,248
Two extreme x_i's eliminated, nonweighted:					
Production rate, metric tons/day (as 100% ammonium nitrate)	51	1,000	320	261	201
Wastewater flow, m^3/s	0.0004	0.2174	0.0354	0.0525	0.0179
Ratio of wastewater flow to production rate, m^3/metric ton	0.15	83.9	14.0	19.1	3.22
Waste NH_3-N:					
g nitrogen/metric ton	8	6,180	1,020	1,690	245
g nitrogen/day	2,580	1,300,000	229,000	337,000	115,000
Waste ORG-N:					
g nitrogen/metric ton	22	4,460	532	1,032	161
g nitrogen/day	1,990	3,240,000	92,000	108,000	517,000
Wastewater concentration, g nitrogen/m^3:					
NH_3-N	5	495	134	127	88
ORC-N	1	1,170	129	280	29
1-Yr receiving water flow, m^3/s:					
Low	0.5	5,975	1,484	2,440	347
Mean	68	17,896	4,549	7,261	1,248

TABLE 5. CALCULATED STATISTICAL PARAMETERS CHARACTERIZING WASTEWATER STREAMS FROM AMMONIUM NITRATE PLANTS

	Mean	Standard deviation
All x_i's, weighted:		
Wastewater flow, m^3/s	0.0508	0.115
Waste NH_3-N:		
g nitrogen/metric ton	1,030	1,560
g nitrogen/day	410,000	827,000
Waste NO_3^--N:		
g nitrogen/metric ton	472	563
g nitrogen/day	197,000	290,000
Wastewater concentration, g nitrogen/m^3:		
NH_3-N	608	1,460
NO_3^--N	376	1,490
1-Yr receiving water flow, m^3/s:		
Low	914	2,667
Mean	2,922	7,515
Two extreme x_i's eliminated, weighted:		
Wastewater flow, m^3/s	0.0327	0.0482
Waste NH_3-N:		
g nitrogen/metric ton	862	1,190
g nitrogen/day	377,000	809,000
Waste NO_3^--N:		
g nitrogen/metric ton	471	556
g nitrogen/day	181,000	270,000
Wastewater concentration, g nitrogen/m^3:		
NH_3-N	482	1,270
NO_3^--N	121	157
1-Yr receiving water flow, m^3/s:		
Low	771	2,564
Mean	1,985	7,628

TABLE B-6. CALCULATED STATISTICAL PARAMETERS CHARACTERIZING WASTEWATER STREAMS FROM UREA PLANTS

	Mean	Standard deviation
All x_i's, weighted:		
Wastewater flow, m^3/s	0.0499	0.0727
Waste NH_3-N:		
g nitrogen/metric ton	838	1,340
g nitrogen/day	334,000	629,000
Waste ORG-N:		
g nitrogen/metric ton	580	1,410
g nitrogen/day	139,000	211,000
Wastewater concentration, g nitrogen/m^3:		
NH_3-N	135	171
ORG-N	148	320
1-Yr receiving water flow, m^3/s:		
Low	2,735	5,472
Mean	8,273	16,356
Two extreme x_i's eliminated, weighted:		
Wastewater flow, m^3/s	0.0399	0.0560
Waste NH_3-N:		
g nitrogen/metric ton	756	1,270
g nitrogen/day	279,000	567,000
Waste ORG-N:		
g nitrogen/metric ton	275	301
g nitrogen/day	104,000	148,000
Wastewater concentration, g nitrogen/m^3:		
NH_3-N	120	155
ORG-N	90	188
1-Yr receiving water flow, m^3/s:		
Low	2,728	5,688
Mean	8,889	18,394

A maximum, minimum, mean, standard deviation, and median were generated for each column appearing in Tables B-1 and B-2. In addition, the same statistical parameters were derived after eliminating the minimum and maximum in each column of data. These statistical parameters are listed in Tables B-3 and B-4.

Weighted statistical parameters were also generated for each column using the fraction of the total production rate of all plants considered as the weighing factor. Using the statistical method, values associated with the largest plants would have a greater impact on the derivation of the statistical parameter. The following equations were used to calculate weighted means and weighted standard deviations:

$$\bar{x} = \sum_{i=1}^{n} \left[\left(\frac{w_i}{\sum_{j=1}^{n} w_j} \right) (x_i) \right] \tag{B-11}$$

$$s = \left\{ \frac{\sum_{i=1}^{n} \left[\left(\frac{w_i}{\sum_{j=1}^{n} w_j} \right) (x_i)\ (n) - \bar{x} \right]^2}{n-1} \right\}^{1/2} \tag{B-12}$$

where $\bar{x}$ = arithmetic mean
s = standard deviation
n = number of samples
w_i = plant output corresponding with x_i, metric tons/day
w_j = plant output, metric tons/day
x_i = individual of the column for which the statistical parameter is being calculated

Units for x_i are given in Table B-7.

Weighted means and standard deviations were also calculated after eliminating the maximum and minimum value of x_i in each column of Tables B-1 and B-2. These statistical parameters are presented in Tables B-5 and B-6.

TABLE B-7. UNITS FOR x_i

Parameter	Units
Wastewater flow	m^3/s
Nitrogen waste flow	$\frac{g\ NH_3\text{-}N}{metric\ ton}$, $\frac{g\ NO_3^-\text{-}N}{metric\ ton}$, $\frac{g\ Org\text{-}N}{metric\ ton}$
	$\frac{g\ NH_3\text{-}N}{day}$, $\frac{g\ NO_3^-\text{-}N}{day}$, $\frac{g\ Org\text{-}N}{day}$
Concentration	$\frac{g\ NH_3\text{-}N}{m^3}$, $\frac{g\ NO_3^-\text{-}N}{m^3}$, $\frac{g\ Org\text{-}N}{m^3}$
Flow/output ratio	$\frac{m^3}{metric\ ton}$

GLOSSARY

air stripping: Wastewater treatment process in which, as applied to nitrogen fertilizer effluents, air is passed countercurrent to a wastewater stream in a column or stripping tower to remove ammonia.

biological treatment: Wastewater treatment process which, as applied to nitrogen fertilizer effluent, employs biological nitrification to aerobically oxidize ammonia to nitrate, and biological denitrification to anaerobically reduce nitrate to nitrogen gas.

carbon monoxide shift: High and low temperature catalytic reaction in which steam is added to transform carbon monoxide to carbon dioxide and hydrogen in the production of synthetic ammonia.

containment: Wastewater control technology in which effluent is collected, held, and may or may not be drained.

desulfurization: Removal of hydrogen sulfide from natural gas feedstock, prior to reforming, by use of an activated carbon or zinc oxide bed in the production of synthetic ammonia.

graining: Process in which concentrated solution is solidified by placing it in a steam jacket-heated kettle and mixing until the water evaporates.

granulation: Process in which concentrated solution is solidified by spraying it on a falling curtain or rolling bed of seed particles to build a larger particle.

hazard factor: Concentration of a particular pollutant in water which has been determined to be hazardous to aquatic life.

high density prills: Prills formed using a 99.5+% solution that lowers the number of void spaces formed to create a more dense prill.

ion exchange: Wastewater treatment process by which an ion in the wastewater is exchanged for a more desirable counterion on a resin in a column or bed.

low density prill: Prills formed using a 95% to 96% solution that allows more voids in the final product, giving a less dense prill.

methanation: Catalytic reaction in which hydrogen in process gas converts trace amounts of carbon monoxide and carbon dioxide to methane and water in the production of synthetic ammonia.

prill: Spherical particle formed by the solidification of solution droplet.

prilling: Process in which concentrated solution is solidified by spraying it in a tower so that the drops formed fall countercurrent to a stream of cooling air.

primary reformer: Set of catalyst-filled tubes in which natural gas (methane) reacts with steam to form carbon monoxide and hydrogen in the production of synthetic ammonia.

secondary reformer: Catalytic reactor in which compressed air is mixed with process gas from primary reformer to produce a synthesis gas with a hydrogen-to-nitrogen mole ratio of 3:1 in the production of synthetic ammonia.

source severity: Ratio of the concentration of a given pollutant in the receiving water as a result of discharge to the minimum concentration of the pollutant determined to be hazardous (hazard factor).

steam stripping: Process in which process condensate flows down a column countercurrent to steam which extracts ammonia and methanol from condensate.

urea hydrolysis: Process in which urea in condensate is converted through a series of intermediate products back to ammonia and carbon dioxide, which are then driven off with steam.

CONVERSION FACTORS AND METRIC PREFIXES (83)

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit (°F)	$t_{°F} = 1.8\ t_{°C} + 32$
Gram (g)	Pound-mass	2.205×10^{-3}
Joule (J)	British thermal unit (Btu)	9.479×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilogram (kg)	Ton (short, 2,000 lb mass)	1.102×10^{-3}
Kilogram/meter^3 (kg/m^3)	Pound-mass/gallon (lb-m/gal)	8.348×10^{-3}
Kilometer^2 (km^2)	Mile^2	3.861×10^{-1}
Meter (m)	Foot	3.281
Meter^3 (m^3)	Foot^3	3.531×10^{3}
Meter^3	Liter	1.000×10^{3}
Meter^3/second (m^3/s)	Gallon/minute (gpm)	1.585×10^{4}
Metric ton	Ton (short, 2,000 lb mass)	1.102
Pascal (Pa)	Atmosphere	9.869×10^{-6}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Second (s)	Minute	1.667×10^{-2}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Mega	M	10^6	5 MPa = 5×10^6 pascals
Kilo	k	10^3	5 kg = 5×10^3 grams
Milli	m	10^{-3}	5 mg = 5×10^{-3} gram
Micro	μ	10^{-6}	5 μg = 5×10^{-6} gram

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(83) Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.